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DYNAMICS OF A GRAY LUVISOL

by

© ROBERT W. HOWITT

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF

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IN

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Submitted by

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ABSTRACT

An undisturbed site under forest cover adjacent to the Breton Plots, Breton, Alberta, was chosen to study the dynamics of a Gray Luvisol. Soil moisture and temperature were monitored at selected depths over a two-year study period. Canopy drip collectors and gravity lysimeters were used to study nutrient movement and the process of lessivage.

It was found that the order of cation concentration for canopy drip and lysimeter samples was K, Ca, Na, and Mg, except in the Bt lysimeter samples where the order was Na, Ca, K, and Mg. Concentration due to evapotranspiration and cation retention resulted in changes in concentration of cations as water leached through the solum.

The results indicate water movement into the Ae horizon is inhibited by the LFH horizon. It was found that ice lensing in winter enhances the platy structure of the Ae horizon.

This study revealed that under present day conditions micaceous clays are being illuviated into the upper Bt horizon. Fine clay sized smectite migrated into the lower solum during earlier stages of soil genesis. It was found that lessivage involves the movement of Fe, Al, and organic constituents both in solution and in colloidal form. The concentrations of these elements is a function of the rate of water movement whereas the concentration of other cations is independent of the rate of water movement.

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CHAPTER I

INTRODUCTION

Studies of soil genesis have, in the past, focused on the five factors of soil formation: vegetation, climate, parent material, relief, and, time. In other words, the reorganization of soil materials has been related to or explained by these five factors. Another approach has been to study the actual processes responsible for soil formation. For example, the process of 'podzolization' has been studied extensively. Generally pedogenic processes and their mechanisms have been inferred from the careful examination of pedon, chemical, physical and mineralogical properties (Ugolini 1978). Ugolini (1978) termed this type of research as "static pedology" as opposed to "dynamic pedology," which is the study of pedogenic processes in situ.

A pedon adjacent to the Breton Plots, Breton, Alberta, was chosen for a study of the dynamics of the Luvisolic soil system with special reference to clay migration.

The dynamics of the Gray Luvisol under forest cover are unclear. Temperature and moisture regimes, though not well documented, are of considerable importance to pedogeneses. The process of clay migration is not clearly understood. Although theories have been proposed, none have been thoroughly investigated or substantiated.

The mechanism of clay migration may be purely physical;

clays being peptized by freezing and thawing and wetting and drying cycles then washed downward to be deposited in the Bt horizon. It has also been suggested that the process may be mediated by organic compounds. Conclusive evidence for either theory is lacking and the mechanism of the latter is unclear.

This thesis has been divided into two sections. The first entitled "Static Pedology" is a study of the chemical, physical, and mineralogical characteristics of the pedon. The object of this section is to establish the pedogenic changes which have occurred to date as recorded in the morphological features and soil properties. The second portion deals with the dynamics of this particular pedon and is entitled "Dynamic Pedology." The objectives of this section are four-fold:

1. to determine zones of eluviation-illuviation;
2. to determine the nature of soil components that are migrating within the pedon;
3. to quantify seasonal changes in soil moisture and temperature regimes of the Orthic Gray Luvisol under forest cover; and
4. to obtain information about weathering and mineral alteration and nutrient cycling.

It is intended, then, to elucidate the mechanisms of pedogenesis of Gray Luvisols on the basis of all accumulated data.

CHAPTER II

LITERATURE REVIEW

GENERAL

In Canada, Luvisolic soils are defined as soils having light coloured eluvial horizons and illuvial B horizons in which silicate clay has accumulated. The argillic horizon is one in which there is an enrichment of silicate clay that has been transferred from the A horizon to the B horizon by physical processes without chemical alteration. This horizon is diagnostic for Luvisolic soils throughout the world.

Luvisolic soils are found on most major continents and are defined in most systems of soil classification. In the FAO/UNESCO soil classification of the world Luvisols are defined as soils having argillic horizons, which have a base saturation of 50% or more and lacking the diagnostic horizons of other soil orders. Luvisols fall into the Alfisol Order of Soil Taxonomy; the boreal Luvisols which are common in Canada are referred to as Boralfs in Soil Taxonomy. The French use the term Sol Lessivé to describe boreal soils with argillic horizons whereas the Russians call similar soils Gray Forest soils and in the German System of Soil Classification these soils are referred to as Parabraunerde.

Luvisolic soils are found in many climatic regions around the world from cool moist and moderate moist regions in the northern hemisphere and on all continents in subhumid and

mediterranean climates. The most extensive areas of Luvisolic soils are found in humid and subhumid regions on young parent material that has been stable and free from pedoturbations for several thousand years. The parent materials are young enough that they contain notable amounts of clays, bases and minerals. Luvisols are present in vast areas of existing or former deciduous forest land on till, loess, lacusrine and fluvial materials. In tropical areas they exist on the younger geomorphic landscapes while older landscapes are occupied by Ultisols and Oxisols.

In Canada these soils are common in subhumid to humid, mild to very cold climates, on sandy to clayey, base rich, parent materials. The largest area of these soils occurs in the central to northern Interior Plains. The Gray Luvisols of this area are characterized by well developed platy Ae horizons, Bt horizons with moderate to strong blocky mesostructure, and calcareous C horizons. These soils have developed on high base status parent materials under deciduous, coniferous and mixed forest on level to hilly topography.

THE GENESIS OF LUVISOLIC SOILS

For some time the genesis of soils has been considered to be a function of the factors of soil formation. Boul et al. (1973) define a factor of soil formation as "an agent, force, condition or relationship, or combination of these, which influences, has influenced, or may influence a parent material of a soil, with the potential of changing it." The factors of soil formation are

considered to be climate, vegetation, parent material, relief, and time. Other forces have been considered as factors of soil formation, for example, water, gravity, and man as proposed by Rode (1961). The five generally accepted factors have been divided into two groups, active factors and passive factors. The active factors are vegetation and climate, while parent material and relief are considered as passive factors. Time is required for a steady state to be obtained (Twardy 1969; Lavkulich 1969).

As a first approximation, I will consider the genesis of Luvisolic soils in the light of these factors. In Alberta, Luvisolic soils are found under boreal forest, in the dry subhumid moisture region as defined by Rowe (1972).

Of the five factors of soil formation, climate and vegetation appear to play the most important role in the genesis of Luvisolic soils. The influence of these two factors are inextricably linked and their influence on soil development cannot be separated. The influence of vegetation is discussed by Pettapiece (1969) in a study of the forest-grassland transition. It is noted that Luvisolic soils are found in areas where mixed forest has been dominant, whereas Chernozemic soils are found in areas where grassland vegetation has been dominant for some time. Under grassland regimes, Ca is thought to be cycled from the subsoil to the upper solum, and large volumes of organic C are thought to be added yearly to the A horizon. Conversely, under boreal forest, it is thought that Ca is depleted from the upper solum by leaching and is not cycled by the plants, resulting in moderately acid conditions. Much less organic matter

is added in the form of leaves and much of the organic matter is mineralized rapidly to small molecular weight organic acids (Pettapiece 1969). The possible effects of these organic acids on pedogenesis will be discussed in a later section.

Climate has a significant effect on vegetation. Luvisolic soils are found at somewhat higher elevations (or latitudes). As elevation (or latitude) increases, the mean annual temperature decreases. For example, the Breton Plots, the location of this study, are found some 150 meters above the plain where Chernozemic soils are found. The predominance of aspen poplar and white spruce may be a result of the change in climate. This relationship of elevation, vegetation, and soil is also found on the Cooking Lake moraine and the Duffield moraine.

Argillic horizons are found in areas where there is a dry period for some portion of the year (subhumid moisture regimes) (Soil Taxonomy 1978). The drying and subsequent rewetting of these soils likely plays a role in the accumulation of clay in Bt horizons. This point will be discussed in a later section.

Climate and vegetation are considered active factors of soil formation as they constitute forces which directly influence parent geological materials. Vegetation is particularly important in that it produces the organic matter which is incorporated into the soil and has such variable properties that are reflected in soil morphology. Parent material and relief are considered to be passive factors of soil formation. Parent material acts as a source of original material and distributing agent of the other processes (Twardy 1969). Texture, structure, and chemistry of

parent materials may strongly influence soil development.

Lessivage is the term used to describe the physical movement of clay, without destruction from the upper portion of the solum to the lower solum. Rode (1961) coined the term illimerization to describe this soil forming process as being a distinctly separate process from podzolization. For many years Russian authors did not separate lessivage from podzolization when considering soil genesis. Zonn (1973) identifies Brown Forest - Lessivé soils and Brown-Pseudopodzolic soils as being different from true Podzolic soils. They differ by lacking adequate evidence of a) the destruction of primary and secondary minerals, and b) of the accumulation of silica which are the two phenomena so characteristic of podzolization (Rode 1964).

Zonn (1973) is of the opinion that the processes of lessivage and pseudopodzolization have been influenced by variations in composition and structure of glacial and non-glacial deposits. In particular, it is the presence of carbonates in the till that favours accumulation of clay in the B horizon (by flocculation of downward moving clay). Consequently, he states that the occurrence and thickness of the Bt horizon is a function of the depth of occurrence and content of carbonates in the till. In conclusion, he notes that lessivage is favoured by: a vegetative cover of mixed grass, deciduous and coniferous trees; accelerated decomposition of organic matter releasing an abundance of humic acids; presence of geochemical sieves of carbonates and relatively fine textured materials; alternating wet and dry conditions in the upper solum throughout the year;

and seasonal over-moistening of the soil.

In Alberta, most soils have developed from glacial till that at one time was calcareous. Tills of the Alberta Plain, on which Luvisolic soils have developed, tend to be fine textured (loam to clay loam). Lime has been leached to depth and there is rarely any morphological evidence of salinity.

Relief is also considered to be a passive factor in soil formation. Topography or relief affects soil drainage and soil moisture and temperature regimes. In turn, these influence vegetation, biological activity, and rates of inorganic reactions.

Macyk et al. (1978) concluded that soil temperature and soil moisture regime are related to slope position, and that relief and microclimate have a greater influence on soil morphology and related physical properties than on soil chemical properties. Profiles in lower slope positions were shown to exhibit slightly more eluviation than soils in upper slope positions. This was attributed to a greater amount of moisture, in the form of runoff, passing through these profiles.

Time is the last, but by no means the least important, factor of soil formation. Estimates have been made on the time required for a soil to reach steady state with the environment. It is not the amount of time that has passed that is significant; it is the changes that have taken place over time that are important.

Wright et al. (1959) studied the chemical, physical, and mineral characteristics of a chronosequence of soils in the Northwest Territories. The sequence of soils (Regosol - Brunisol -

Luvisol) was located on fine textured fluvial parent materials under a mixed stand of spruce-aspen poplar. In the study it was assumed that climate, vegetation, relief, and parent material were all equal in their influence on soil genesis. Time, then, was the significant factor responsible for the morphological differences between these soils. Their conclusions traced a five step pattern of development:

1. the accumulation of organic matter in the upper part of the calcareous parent material;
2. decomposition of carbonates with calcium being removed twice as quickly as magnesium, followed by the depletion of organic matter;
3. a greater loss of silica than sesquioxides in early stages of development;
4. continued loss of bases, particularly calcium, subsequent to the depletion of carbonates accompanied by a further decrease in pH and further loss of organic matter; and
5. marked eluviation of clay and accelerated leaching of iron and aluminum with respect to silica resulting in a distinct eluviated layer of A2 underlain by a clay sesquioxide enriched layer B.

This paper illustrates clearly the time factor as it relates to the genesis of Luvisolic soils.

It is important to keep in mind that the passage of time may be regarded as constant, but climate, vegetation, and relief may have been very different in times past. In other words the morphological characteristics of soils observed in the present

may be relict of past conditions. The study of soil dynamics, on the other hand, tells us about soil forming processes as they are occurring today.

An analysis of the factors of soil formation as they relate to Luvisolic soils has indicated (in a general sense) where these soils may be found. It does not, however, tell us "how" these soils develop. In other words, this approach to soil genesis does little to elucidate the process by which argillic horizons form or the mechanism of that process. The following discussion reviews current theories regarding the processes of clay migration.

THE PROCESS OF CLAY MIGRATION

Pedogenesis is a function of specific soil forming processes. These processes may or may not be related to factors of soil formation.

A soil forming process is a sequence of complex events that have a definite and observable effect on soil formation. Lessivage is a soil forming process that involves the movement of silicate clays from the upper solum into the lower solum resulting in the formation of an argillic horizon. Generally speaking, a number of these processes are active during the genesis of any given soil.

Duchaufour (1978) ties the morphological characteristics of boreal eluviated soils to three simultaneous processes:

1. eluviation of clay which is the most prominent process;
2. temporary waterlogging which induces reduction and mobilization of iron in the middle horizons; and,

3. more or less intense biochemical weathering of part of the clay minerals with formation of organo-mineral complexes.

The eluviation and illuvation of clay without chemical alteration is considered to be the dominant soil forming process in the genesis of Luvisolic soils. Particle size distribution of Luvisolic soils indicates that mainly fine clay is removed from the zone of degradation, and that argillans in the lower solum are composed mainly of fine clay (Bullock 1968). Further evidence supporting lessivage is the similarity of clay mineral species throughout the Luvisolic profile (Bullock 1968; Wang 1971; Ranney & Beatty 1969; Minashina 1958; Brown et al. 1932).

Oriented clays (argillans) in argillic horizons are also indicative of illuviation of clay as opposed to synthesis of clay minerals. Boul & Hole (1961) conclude that clay skins in Wisconsin soils are formed by the percolation of dilute suspensions of clay, from which the clay is deposited at or below the bottom of the solum as percolation ceases and the larger pores are emptied of water.

Kremner (1969) concludes that the accumulation of clays in argillic horizons is a result of the movement of undecomposed clays. He does not however rule out the possibility of the new formation of clays from dissolved substances. Kremner's study of argillans led him to postulate that seasonal wetting is most likely to be responsible for the restoration and formation of pathways for the migration of clay suspensions. It is in the cracks and cavities that clay deposition occurs.

There have been reports in the literature (Brewer 1968;

Nettleton et al. 1969) that illuvial clay is not the major factor in the genesis of argillic horizons. Nettleton et al. (1969) found that although fine textured Bt horizons of soils in arid and mediterranean climates in Southwestern U.S.A. are highly oriented, distinct illuvial clays cannot be recognized. Brewer (1968) concluded that in some profiles, illuvial clay is insignificant in the formation of argillic horizons. Brewer's study led him to conclude further that in situ weathering, sedimentary layering, or differential weathering between the A and B horizons were more important factors in the genesis of some argillic horizons. It must be remembered that this work was done with soils in tropical environments, very different from the boreal environment of Luvisolic soils in Alberta.

THE MECHANISM OF CLAY MIGRATION

That lessivage is the dominant soil forming process in the genesis of argillic horizons is well documented. It is the mechanism of this process that is not clearly understood.

> "If clay moves from one horizon to another or from one point to another within a horizon, something must start the movement and something must stop it. These processes are poorly understood or at least not a subject of general agreement" (Soil Taxonomy 1978).

The intriguing problem of eluviation-illuviation of clay has been the subject of much study since the earliest days of pedology. The culmination of this study is summarized in Soil Taxonomy 1978. The mechanism proposed therein is based on the

factors of soil formation. It is assumed that:

1. clay is carried by water.
2. clay has migrated as clay and not as products of decomposition that were later synthesized.
3. time is important as argillic horizons are not found on the youngest landscapes.
4. vegetation is important as argillic horizons are expressed more strongly under forest than under grassland.
5. climate is important as argillic horizons are only found where soils are dry or partly dry during some part of the year.

The steps involved in clay migration are:

1. the parent material contains fine clays or weathering produces them.
2. clays are flocculated in the solum due to cation content or salts.
3. wetting of a soil leads to disruption of the fabric and dispersion of clays.
4. dispersed clay moves with percolating water and stops where the water stops.
5. non-capillary water is drawn from the larger voids by capillary withdrawal leaving clays plastered on void walls.

This mechanism is favoured, in several ways, by a seasonal water deficit:

1. wetting favours dispersion.
2. drying cracks form in which water at low tensions can percolate.

3. halting of water by capillary withdrawal is favoured.

This is a mechanism which represents a summary of available information and research. It is supported by the work of many American and European authors.

Smith (1934); Jenny and Smith (1935); and Bray (1935) were the first investigators to study clay migration in an experimental situation. Prior to their investigations Russell and Engle (1925) had proposed the theory, that as soil is leached the surface becomes acidified and deflocculation of clay results from this acidification.

Smith (1934); and Jenny and Smith (1935) propose two mechanisms for clay migration under two different climatic regimes. Based on their experimental work, they propose that under subhumid conditions the depletion of electrolytes and easily soluble compounds from the surface horizon causes the deflocculation of clay. The dispersed clays move downward until they reach a zone where salts have accumulated sufficiently to cause flocculation. The flocculation of clay would cause fine pores to become plugged and as time passed more and more clay would be sieved out mechanically, resulting in a clay increase in the B horizon.

Bray (1935) disagreed with Jenny and Smith. He proposed that the mobilization of clay particles in the soil was due to rapid water movement in the initial stages of a rainfall. He believed that clay mobilization would occur even in the presence of flocculating ions. Deposition of these clays would occur when the force of the water movement was no longer able to overcome

the attraction between the clay and the channel surface.

The concept of sieving of clays in the B horizon is supported by Bodman and Harradine (1939). They found that finer textured soils showed greater clay accumulation than did coarser textured soils. They found that although fine clays were present in coarser textured materials, the clays did not accumulate in the B horizon due to high percolation rates and large pore spaces. Zonn (1973) also suports the "geochemical sieve" theory when considering argillic horizon genesis.

Brewer and Haldane (1957); and Dijkerman et al. (1967) have shown that orientated clays may be prepared by passing suspensions of clay through columns of sand. Dijkerman et al. conclude that clay illuviation may be due to:

1. drying
2. gravitational settling
3. sieving of clays as suspensions move through fine pores

Their results suggest that sieving is only operative if the clay is flocculated (McKeague and St. Arnaud 1969).

Brewer and Haldane (1957) conclude that:

1. the saturating cation has no effect on the degree of clay orientation.
2. illuviation may be accomplished by upper movement of a suspension of clay.
3. if illuviated clay is flocculated in large pore spaces it will be only weakly oriented.
4. if soluble salts are not excessive in the profile, illuviation results in the development of strongly oriented clay bands

and coatings.

5. the presence of silt sized material has a disrupting effect on clay orientation.

It is apparent from this work that argillans develop where downward movement of water stops and is a result of drying. This work suggests that sieving is not as important a mechanism of illuviation as previously supposed.

A fair amount of study has centered around the illuviation of clay in B horizons and clay skin genesis. There appears to be little controversy in the literature regarding the mode of clay deposition in the lower solum. There does however appear to be some discussion with regard to the mechanism by which clay is mobilized in the surface horizons. As stated in Soil Taxonomy 1978 the generally accepted mechanism of clay mobilization involves dispersion of clay by wetting. It has been postulated that freeze-thaw cycles may be also be responsible for the initial dispersion of clays in the process of lessivage.

It has also been suggested in the literature that soluble organic compounds may mobilize clays (McKeague and St. Arnaud 1969; Pettapiece 1969; Davis 1971; Kremner 1969; Mel'nikova and Kovenya 1974ab). The role of soluble organics in the process of podzolization has been documented (Dawson et al. 1978; Adams and Boyle 1979; McKeague and St. Arnaud 1969; Davis 1971; Ugolini et al. 1977; and Ponomareva 1969). Their role in the process of lessivage is less clear.

That clay minerals and organic compounds interact is well documented (Schnitzer and Kodama 1966, 1972, 1976, 1977; Theng

1976; Greenland 1971; and Davis 1971). These interactions take two forms, the first is dissolution and the second adsorption. Dissolution reactions are of significance to the podzolic process whereas adsorption reactions are probably of importance to the process of lessivage.

Adsorption reactions of clay minerals and organic compounds have been reported to have a stabilizing effect on soils. In particular this stabilizing effect is reported in regard to Chernozemic soils. Other work suggests a destabilizing effect of organic compounds on soil.

Bloomfield (1954, 1956, and 1963) has studied the deflocculative effect of aqueous leaf extracts of a number of deciduous and coniferous trees on kaolinite. Aspen poplar was one species studied that dispersed kaolinite. A similar reaction is noted for montmorillinite, however there is apparently a flocculative-deflocculative effect which is proportional to the concentration of leaf extracts.

Bloomfield (1954 and 1963) speculates that polyphenolic compounds from leaf extracts cause deflocculation of clay minerals by sorption and that this reaction may be responsible for clay mobilization. In the 1963 paper Bloomfield concludes that polyphenols are responsible for soil dispersion whereas polysaccharides are responsible for soil stability. This theory is supported by the work of Dormaar (1971).

Dormaar set up columns of Chernozemic material which were leached with aqueous extracts of aspen or black poplar for a period of two years. It was found that aspen poplar extracts

caused greater changes in the Ah material than did black poplar extracts, which in turn were more effective than distilled water. The most significant changes were in pH, exchangeable Ca, and O.IN NaOH extractable C. This work does not consider the mobilization of clay, however it clearly demonstrates the destabilizating effect of aspen poplar on soil aggregates as suggested by Bloomfield (1963).

Leaching experiments performed by Thorp et al. (1957) demonstrate that leaching of crumbled Bt material with organic acids produces visibly bleached A horizons and corresponding B horizons. Variable quantities of cations (Ca, Mg, K, Na, Fe, Mn, P) were mobilized and detected in the leachates. Detectable quantities of fine silicate clay were found in the leachate. It must be remembered that much of this work is the result of strong (O.IN) solutions of oxalic and tannic acids. Experiments with deciduous (maple and beach) leaves, by the same authors, produced similar results but to a lesser degree.

The Russian scientists Mel'nikova and Kovenya (1974ab) studied the movement of labelled clay particles in soil monoliths in relation to the physiochemical properties of the soil. In particular they were interested in the effect of pH of the leaching solution, and the presence of mobile iron and organic matter in the profile on the mobility of vermiculite. They found that at pH values of 5.0 and 6.3 clays migrated most rapidly and penetrated deepest into the soil column. They consider a close to neutral medium to be most favourable to clay migration. They found clays saturated with iron showed very little mobility,

however when fulvic acid was added to the medium, mobility increased. When fulvic acid was added to non-saturated clay the greatest mobility was noted. Their conclusion was that a slightly acid reaction and the presence of mobile organic matter favours clay migration. They postulate that fulvic acids play a protective role with respect to the dispersed state of clay.

Souchier and Duchaufour (1969) envisage the fixation of soluble organic compounds on clay particles as being responsible for the stability of clay suspensions in acid conditions (from Gombeer and D'Hoore 1971).

It is the conclusion of Kremner (1969) that the peptizing effect of organic solutions on clays in the soil is to some degree responsible for the migration of clay. It is apparent from his work that this conclusion is not based on his micromorphological studies. It does, however, indicate that the idea of clay mobilization resulting from organic peptization is held by many authors. It has in fact been suggested on many occasions, without experimental results, that this mechanism is operative in the genesis of Luvisolic soils.

One must conclude from the foregoing that there is evidence to support the theory that soluble organic matter may mobilize clays. It is apparent that organic acids are capable of deflocculating clays and tend to destabilize soil materials. As yet however, conclusive evidence to support the hypothesis that organic acids are responsible for clay movement in Luvisolic soils has not been provided.

One must conclude from examining this work that vegetation

plays a significant role in the genesis of Luvisolic soils. It appears that organic acids (polyphenols) deflocculate clays, generally have a destabilizing effect on soil forming materials, and may be responsible for the mobilization of clay in the process of lessivage.

Careful study of argillans and ped exteriors, as compared to ped interiors, from argillic horizons has also suggested that organic components are involved in clay migration.

Heil and Buntley (1965); and Boul and Hole (1959) both report finding higher quantities of organic C and N in material from ped surfaces as compared to ped interiors. Boul and Hole report a C content of 1.86%, more than four times the content of the ped interior. Khalifa and Boul (1968) found a greater quantity of N in the clay skins than in bulk soil samples. Grossman et al. (1964) did not analyze for C and N, however they found that collapse of d-spacing from 14 angstroms to 10 angstroms was less complete on heating to 450°C for clays from the ped exteriors than for clays from ped interiors. This resistance to collapse might have been the result of interlayer Al-hydroxy groups (chloritization) or it might have been due to interference by organic constituents.

Schnitzer and Kodama (1977) have studied the interactions of clay minerals, particularly montmorillonite, and fulvic acids under laborataory conditions. Much of this work is summarized in their 1977 paper. They have found that interlayer adsorption of fulvic acid by montmorillonite occurs at low pH and is influenced by the cation saturation of the clay. They show by

means of differential thermal analyses that the organic constituents may be protected by the clay mineral at relatively high temperatures. They believe the interference of fulvic acid with the interlayer of montmorillonite tends to increase d-spacings and prevent complete collapse of the mineral on heating.

Perhaps the mechanism by which organic acids increase d-spacing of expandible minerals is best expressed by Perez Rodiquez et al. (1977). They conceptualize surface adsorption of organic acids as being important. Interlayer expansion is considered a result of portions of the organic molecule being attracted to interlayer exchange sites. The molecule as a whole does not move to satisfy these attractions, only portions bend or adjust themselves to the interlayer position. It must be remembered that organic molecules are by no means rigid entities as are inorganic molecules and silicate clays.

Schnitzer and Gupta (1964) in a study of the chemical characteristics of the organic matter of Luvisolic soils found that extraction and purification of organic matter from the Bt horizon was very difficult. This was attributed to the intimate association of the organic fraction with clay minerals. They also note that extracts from the Bt horizon were dominantly (90%) fulvic acid as compared to the LFH horizons where extracts were found to be dominantly humic acids. This work shows that in Bt horizons fulvic acids and clays are intimately associated. That is not to say that the fulvic acid is responsible for clay mobilization. It may be that clay minerals and organic acids

migrate independently and form complexes in the Bt horizon. This later suggestion is not entirely logical considering the reactivity of both clays and organic acids.

A number of researchers have studied naturally occurring clay-organic complexes (Moum et al. 1973; Perez Rodriquez 1976; Anderson et al. 1974; and Dudas 1968). Even with modern techniques such as electron microscopy it is very difficult to show conclusively that clay-organic complexes occur in nature.

Many laboratory studies have been used to show that these compounds may exist (Chen and Schnitzer 1976; Schnitzer and Kodama 1966, 1968, 1971, 1972; and Schnitzer 1969). These are artificially created compounds and do not prove that such complexes exist in nature. It is difficult however to imagine that they do not occur in nature given the ease with which they interact in the laboratory.

In summary it has been indicated that some controversy about the role of organic compounds in the mobilization of clay is found in the literature. To date there is no conclusive evidence to suggest that organic compounds are responsible for clay mobilization.

There is little doubt, based on the literature, that wet-dry, freeze-thaw cycles may be responsible for clay migration in Luvisolic soils. It remains to be shown whether or not organic acids mediate this process. Consequently the working hypothesis of this thesis is that organic acids do not play a significant role in clay mobilization.

SOIL MOISTURE AND SOIL TEMPERATURE REGIMES

Soil moisture and temperature, as influenced by climate are of significance to soil genesis. The rates of organic and inorganic soil reactions are to a very large degree determined by soil temperature and the availability of moisture.

To some extent soil temperature has been used as criteria in the classification of soils in Canada and the U.S.A. For example, it is stated that the mean annual soil temperature of Orthic Gray Luvisols is less than 8°C, while the mean annual soil temperature for Gray Brown Luvisols is greater than 8°C (Canada Soil Survey Committee 1978).

The moisture regime of Luvisolic soils may play a role in lessivage. It has been suggested by Zonn (1978); Duchaufour (1971); and Pomarvenova (1969), that temporary waterlogging of the Ae horizon creates reducing conditions. This temporary reduction may be responsible for the mobilization of iron compounds and of clay in the process of lessivage. It has also been reported (Soil Taxonomy 1978); that argillic horizons are found in areas subject to a seasonal dry period. This drying and subsequent wetting is regarded as the major factor in the mobilization of clays (Soil Taxonomy 1978; Kremner 1974).

Freeze-thaw cycles have also been reputed to be responsible for clay mobilization. Consequently the study of the soil moisture and soil temperature regime of the Luvisolic soil is deemed essential to a study of soil dynamics.

It must be noted that in the case of Ultisols it is believed that lessivage is an active soil forming process. However,

Ultisols are found in tropical areas where seasonal moisture deficits and freeze-thaw cycles are not operational. If clay migration also occurs without wet-dry and freeze-thaw cycles, then some other mechanism must be involved in the translocation of clay.

CHAPTER III

MATERIALS AND METHODS

FIELD SAMPLING

A wooded site adjacent to the Breton Plots, Breton, Alberta was chosen as being representative of an undisturbed Luvisolic soil under native vegetation (Figure 1). A large pit (1.2 m x 2.5 m x 1.8 m) was excavated to facilitate study and sampling of the profile. Bulk soil samples were taken from each of the genetic horizons to a depth of 2 meters. The bulk samples were air dried, crushed, passed through a 2 mm sieve, mixed, and stored for analysis. A profile description of the soil at the Breton Bush Site is found in Table 1.

A soil monolith was taken from the pit using monolith boxes 7 cm x 7 cm x 50 cm in size. After drying the monolith was impregnated using 3M electrical resin. When cured the impregnated monoliths were cut into blocks 5 cm x 5 cm, taking care to observe the proper orientation of each block. One face of each block was polished, glued to a glass slide using epoxy resin, then cut off leaving the glass slide with a thin slice of soil. Each slide was hand ground using various grinding compounds until the slice of soil was highly polished and 30 micrometres in thickness. Cover slips were attached to protect the thin sections. Slides used for micromorphological analysis were the large 5 x 7 cm variety. Thin sections were examined

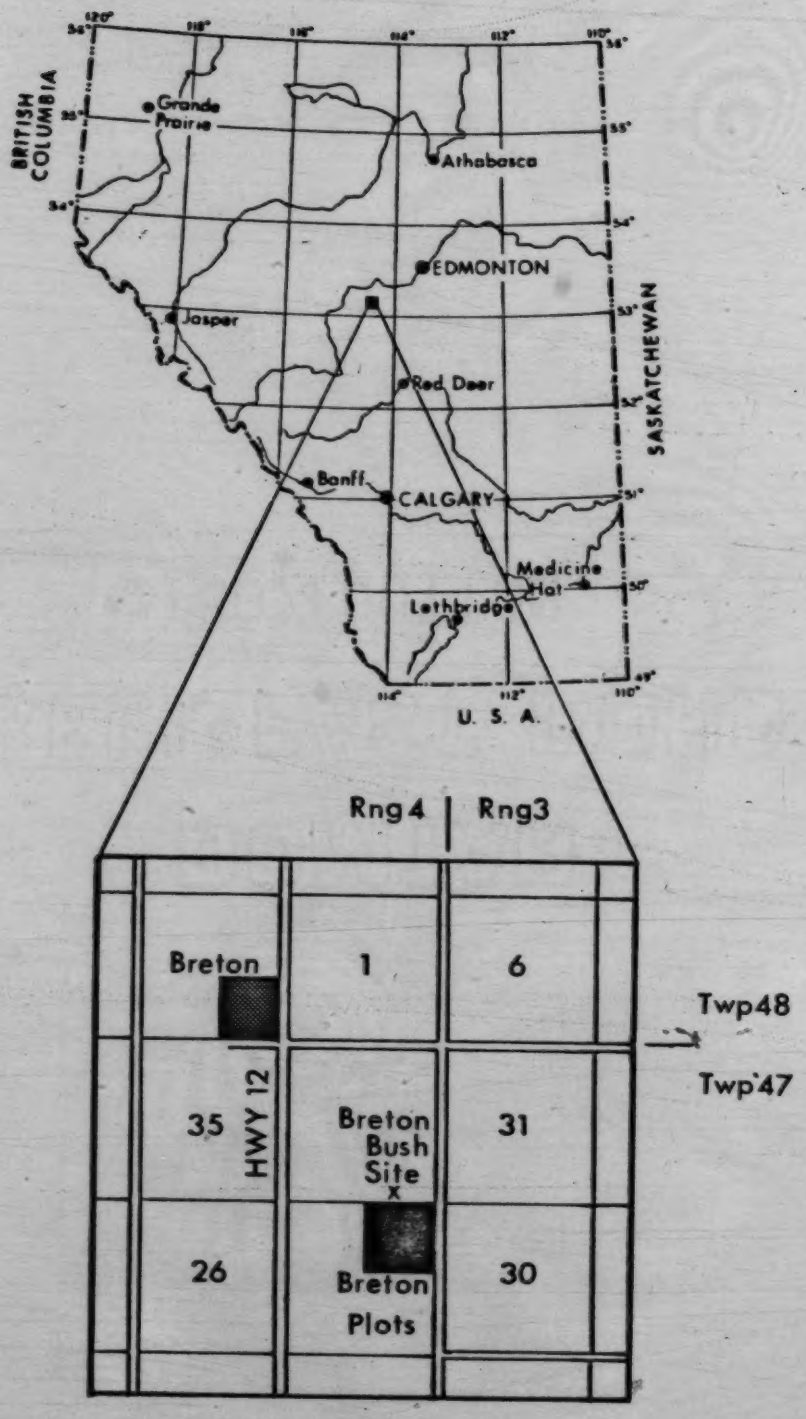


Figure 1. Location map of the Breton bush site.

using a petrographic microscope and described using the terminology of Brewer (1964); and Brewer and Pawluk (1975).

SITE INSTRUMENTATION

The Breton Bush Site was monitored over a two year period for soil moisture and soil temperature. Fiberglass soil moisture cells, manufactured by Soil Test Inc. Illinois were used to evaluate the moisture regime in each of the major soil horizons (LFH, Ae, Bt, C) and at a depth of 228 cm. The cells were calibrated in the laboratory as suggested in the Soil Test manual in order to establish a graphical relationship between soil moisture content and electrical resistance.

The cells were installed at the Breton Bush Site using a 4.5 cm hand auger. Holes were augered to appropriate depth, the cells placed horizontally in the bottom of the hole, and the original material was firmly packed back into the hole. Several weeks were allowed for equilibration. Measurements were taken on a weekly basis from May to October in the years 1977 and 1978. In the winter of 1978 readings were taken on a monthly basis.

A G160 Soil Test thermister temperature probe was used to monitor soil temperature at the site. The probe was wrapped with black electrical tape and tested for accuracy at room temperature and in a freezer, before installation. To install the probe a 4.5 cm hole was augered to a depth of 190 cm, the probe inserted, and the original soil material packed around the probe. Temperature measurements were conducted weekly from May

to October in the years 1977 and 1978 and once a month during the winter of 1978. Measurements were taken at 2.53 cm increments from 0 to 91 cm and at 10 cm increments from 91 cm to 190 cm.

A groundwater well was also installed at the site. This was a 4.5 cm outside diameter pipe with holes drilled in the lower 400 cm. The pipe was installed to a depth of 425 cm and the depth to the water table was measured by means of an electrical resistant device attached to a graduated wire. Readings were taken at weekly intervals.

In order to collect samples of rainwater that had passed through the plant canopy, canopy drip collectors constructed of polyethylene jugs and funnels were also installed at the site. Collectors were placed under both aspen and spruce trees. The collected samples were analyzed for major cations and organic constituents.

Gravity lysimeters were installed under the LFH and Ae horizons and in the upper Bt horizon to collect samples of soil solution leaching through the pedon. The lysimeters were constructed of 10 cm acrylic tubing with 0.6 cm walls. A steel cutting edge and cap were designed to facilitate installation and removal of the tubes. They were forced into the soil using a Giddings hydraulic soil sampler mounted on a truck. The hydraulic soil sampler was also used to remove the tube from the ground.

Upon removal of the soil filled tube the lower 10 cm of soil was removed from the tube, a collector was installed and secured

to the bottom of the soil column. Sand size plastic beads were used in the upper portion of the collection device to facilitate water movement from the soil into the collector. A diagramatic representation of the collection device in place in the lysimeter is presented in Figure 2.

Edge flow effects were corrected for in two ways. First, the cutting edge and method of installation ensured a close, tight fit between the soil and lysimeter wall. Second, the collector is somewhat smaller in diameter than the soil column such that water flowing between the wall of the lysimeter and the soil would not enter the collection reservoir.

Water trapped in the collection reservoir was pumped out by means of a plastic tube affixed to the bottom of the collector. This tube was strung outside the lysimeter to the soil surface. Samples were collected whenever leachate was present in the lysimeter.

PHYSICAL AND CHEMICAL ANALYSES

Procedures followed for soil analysis were generally those outlined by the Canada Soil Survey Committee.

Total cation exchange capacity for the bulk soil was determined using the NH_4OAc method as described by McKeague (1978). Exchangeable cations displaced by NH_4OAc were determined by atomic adsorption spectroscopy (Pawluk 1967).

Particle size distribution was determined using the pipette method as described by McKeague (1978). The methods outlined by McKeague (1978) were also used for the determination of pH

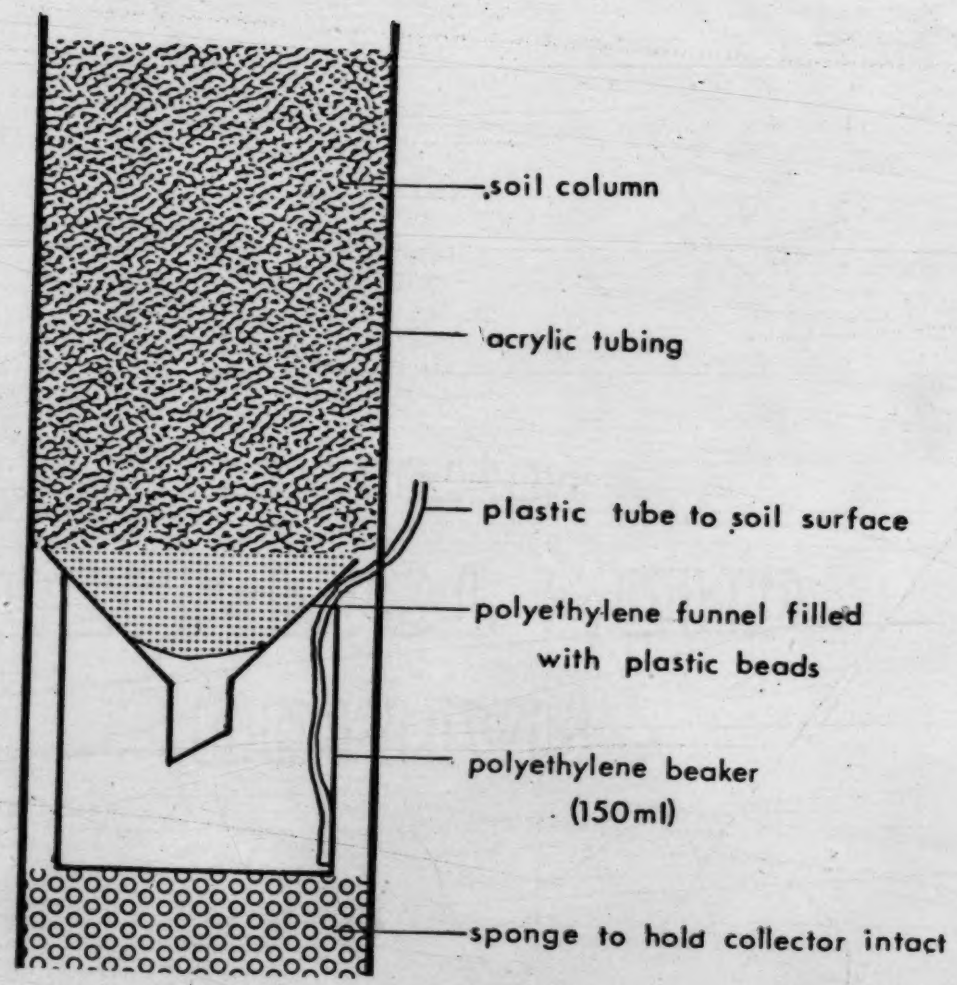


Figure 2. Diagramatic representation of a lysimeter.

in 0.01 M $CaCl_2$ and total exchange acidity using the $Ba(OAc)_2$ procedure.

Total organic carbon for bulk samples was assayed using the wet oxidation technique (modified Wakley-Black) (McKeague 1978). Total N was also determined using the method as outlined by McKeague (1978). The sodium pyrophosphate extraction as described by McKeague (1978) was used to determine amounts of organic complexed Al and Fe for each horizon. The dithionite-citrate-bicarbonate method (McKeague 1978) was used to assay the amounts of "free" (non-silicate) Fe and Al for each horizon. Atomic adsorption spectroscopy was used in conjunction with these methods for determination of Fe and Al in extracted solutions.

Bulk density of the major genetic horizons was determined using the core method of McKeague (1978).

MINERALOGICAL ANALYSES

Fractionation

Bulk soil samples were dispersed in 300 ml of distilled water using a Braunsonic 1510 vibrator probe for three minutes at 350 watts (Edwards and Bremner 1967). Following sonification, samples were washed through a 300 mesh sieve to separate sand from the silt and clay. Clay was separated from silt by gravity sedimentation as described by McKeague (1978). Fine clay ($< 0.2\ \mu m$) was separated from the total clay sample by centrifugation as described by Jackson (1956). Clay samples were freeze-dried for storage and subsequent analysis. Sand and silt

fractions were oven dried before storage.

Sand Mineralogy

The sand fraction of each of the horizon samples was separated into a heavy (S.G. $>$ 2.75) and a light (S.G. $<$ 2.75) fraction using heavy liquid (tetrabromoethane) in separatory funnels. Organic matter was removed from surface horizons with H_2O_2 treatment prior to separation. Removal of carbonates was not necessary for any of the samples.

Grain mounts were prepared for the two separates from each horizon. Standard optical techniques (Kerr 1977) were used to identify no less than 350 grains from each slide. These counts were used to determine the percentage of different mineral species in each fraction of each horizon.

Clay Mineral Analysis

Cation exchange capacity of freeze dried clays was determined by saturating the complex with K^+, washing free of chlorides, with water and water-alcohol mixtures, and resaturating with Ca. The amount of displaced K was determined by atomic adsorption spectroscopy.

The surface area of clays was determined by equilibrating Ca-saturated, oven-dry clays with ethyleneglycolmonoethyl ether (EGME) under vacuum for 48 hours. The weight gain due to the uptake of EGME is proportional to surface area of the clay.

Total dissolution of Ca-saturated clays was conducted as described by Pawluk (1967). Samples were ignited at 850°C prior

to HF-HCl dissolution. Atomic adsorption spectroscopy was used to determine K, Fe, Mg, and Al.

Slides of Ca- and K-saturated clays were prepared using the paste method of Theisen and Harward (1962). X-ray diffraction patterns were obtained under controlled humidity using a Phillips diffractometer equipped with a curved crystal monochrometer and Cu K α radiation (40Kv, 20Ma).

Ca-saturated slides were equilibrated at 54% R.H. or with ethylene glycol before X-ray diffraction analysis. K-saturated slides were heated to 105°C and X-ray patterns were obtained while maintaining 0% R.H. in the sample chamber. These same samples were reequilibrated to 54% R.H. and reanalysed to determine the degree of rehydration. Patterns were also obtained after heating to 300°C and to 550°C.

COLLOIDAL LEACHATE AND CANOPY DRIP ANALYSIS

Samples collected from the lysimeters were centrifuged to remove colloidal materials. Liquid samples were analyzed for K, Mg, Ca Na, Fe, and Al using atomic absorption spectroscopy. Silicon was determined colourimetrically using the acid molybdate method of Mullin and Riley (1955). Polyphenol content was determined using the method of Spalding and Duxbury (1977). Polysaccharide content was determined as described by Brink et al. (1959); and Oades (1967). Polyuronide content was determined by the method described by Lynch et al. (1957) with one modification: the sample was layered on top of the acid before mixing following Oades (1967). This modification provided greater

reproductability of results and better standard curves.

Solid colloidal samples, after separation from liquid samples, were analysed by X-ray diffractometry under controlled humidity but without uniform cation saturation. They were subsequently analyzed for pH independent charge following Dudas (1968).

Extraction with $Na_4P_2O_7$ was followed with pH-independent charge determinations. $Na_4P_2O_7$ extracts were analyzed for Fe, Al, and organic carbon using atomic adsorption spectroscopy and wet oxidation respectively. Extraction with acid ammonium oxalate and sodium citrate followed for the 1977 sample. Again Fe and Al in the extracts were determined using atomic adsorption spectroscopy. Results of these extractions suggested that these procedures could be eliminated from the analysis of the 1978 samples. The final treatment of the solid colloidal material was with H_2O_2 to completely remove all organic C. X-ray analysis was performed after each extraction in order to determine mineralogy and changes in peak height and sharpness.

Electron micrographs were obtained of the materials before and after treatments. Elemental composition of these materials was determined using a Kevex X-ray emission system.

C H A P T E R I V

RESULTS AND DISCUSSION

STATIC PEDOLOGY

The genetic history of a given soil has generally been inferred from the chemical, mineralogical, physical, and morphological characteristics of that soil. Singer (1978) refers to this type of study as static pedology. It is assumed that pedogenesis has proceeded uninterrupted over time and that it is continuing today. This approach provides evidence as to the pedogenic changes that have occurred over time and what processes have been dominant.

GENERAL

The soil at the Breton Site is typical of Luvisolic soils found in Alberta and possesses many of the characteristics of the Breton series as described by Lindsay et al. (1968). A profile description is found in Table 1.

Examination of particle size distribution within the profile (Table 2) reveals a definite accumulation of total clay and fine clay in the Bt horizon relative to the Ae and BC horizons. The increase in clay content in the B horizon meets the criteria, as set out in the Canadian System of Soil Classification (CSSC 1978), for textural B horizons. The Ae horizon has less than 15% clay whereas the Bt horizons contain at least 33% total clay. The

Table 1. Description of profile at the Breton bush site.

L	7.6 - 5.1 cm. Leaf litter; undecomposed and semi-decomposed spruce needles and aspen leaves. Some grass roots.
F	5.1 - 1.3 cm. Some decomposed leaves, needles, mixed with grass roots; loose to matted, numerous fungi; abundant fine and very fine random and plentiful medium random roots; clear smooth boundary.
H	1.3 - 0 cm. Decomposed fibrous to matted organic matter; abundant fine and very fine random and plentiful medium random roots; smooth boundary.
Aeh	0 - 2.5 cm. Dark grayish brown (10YR 4/2 m); sandy loam; moderate medium platy to granular; very friable; plentiful medium random roots; abrupt smooth boundary.
Ae1	2.5 - 7.6 cm. Grayish brown (10YR 5/2 m); sandy loam, moderate medium platy; friable to very friable; few to plentiful fine and very fine random and horizontal roots; clear smooth boundary.
Ae2	7.6 - 12.7 cm. Grayish brown (10YR 5/2 m); loamy sand; weak medium platy; vesicular; very friable; few fine to very fine oblique and random roots; abrupt smooth boundary.
AB	12.7 - 16.5 cm. Yellowish brown (10YR 5/4 m); loam to sandy clay loam; coarse platy to blocky; firm; few medium and fine random roots; abrupt smooth boundary.
Bt1	16.5 - 22.8 cm. Yellowish brown (10YR 5/4 m); clay loam; strong fine subangular blocky; friable to firm; few fine random roots; clear smooth boundary.
Bt2	22.8 - 46.8 cm. Brown (10YR 4/3 m); clay loam; strong fine to medium subangular blocky and weakly prismatic; firm; few fine and very fine random roots; gradual smooth boundary.
Bt3	46.8 - 67.0 cm. Dark yellowish brown - olive brown (10YR 4/4 - 2.5Y 4/4 m); clay loam; moderate medium to coarse blocky and weakly prismatic; firm; continuous clay films evident along cleavage faces; very few oblique medium roots.

BC1 67.0 - 81.0 cm. Dark yellowish brown - olive brown (10YR 4/4 - 2.5Y 4/4 m); sandy clay loam to clay loam; weak coarse blocky to fragmental; firm; very few random fine roots; gradual smooth boundary.

BC2 81.0 - 111.3 cm. Dark yellowish brown - olive brown (10YR 4/4 - 2.5Y 4/4 m); sandy clay loam; fragmental glacial till; very few medium to fine horizontal and vertical roots.

BC3 111.3+ cm. Grayish brown (2.5Y 5/4 m); sandy clay to sandy clay loam till.

NOTES: The profile is developed from fairly uniform till, possibly having a thin sandy wash on the surface. The pit site consisted of an aspen poplar to spruce-aspen stand with the pit area immediately below both spruce and aspen however the south end of the pit is under dominantly spruce. The site has good external drainage and is about 30 meters south of a ravine which is about 10 m deep. The site itself is quite level. Internal drainage is moderate with weak mottles evident in the lower solum.

Table 2. Particle size distribution of the Breton profile.

Horizon	% Sand	% Silt	% Clay	% Fine Clay	Fine Clay: Total Clay
Aeh	32	57	11	2	0.18
Ae1	33	59	8	1	0.13
Ae2	37	56	7	1	0.14
AB	37	42	21	7	0.33
Bt1	28	39	33	14	0.42
Bt2	24	42	34	14	0.41
Bt3	28	39	33	15	0.45
BC1	28	41	31	15	0.48
BC2	29	43	28	8	0.29
BC3	32	41	27	9	0.33

bulge in fine clay content in the Bt horizon is notable. There is at least 13% more fine clay in the Bt horizon than in the Ae horizon. The ratio of fine clay to total clay is greater in the B horizon than in the A or BC horizons; this is another characteristic of textural B horizons. These results are comparable to those reported by Lindsay et al. (1968).

There is a negative enrichment of silt and sand in the A horizons. This is a result of clay removal. Values of bulk density (Table 3) are similar to those reported by Heapy (1971). The increase of bulk density of the B horizon compared to the A horizon cannot be attributed to clay migration.

The total cation exchange capacity (Table 5) is a function of clay and organic matter content. Consequently the bulge in total exchange capacity in the Bt horizon parallels the increase in clay content in this horizon. There is a very slight bulge in organic carbon (Table 4) in the Bt horizon which also contributes to the high total exchange capacity.

It should be noted that Ca occupies 70 - 85% of the exchange complex in the Bt horizon while in the Ae horizon it occupies only 50% of the exchange complex. This suggests that Ca is not being cycled as it is in Chernozemic soils. This agrees with the work of Dormaar (1971) who found that aspen leaf extracts were responsible for the removal of Ca and other cations from Chernozemic Ah material.

Results for pyrophosphate extractable Fe and Al and dithionite-citrate-bicarbonate extractable Fe and Al are reported in Table 6. There is a definite increase in the amount of

Table 3. Bulk density of the major horizons of the Breton profile.

Horizon	g/cm^3
Ae	1.48
AB	1.49
Bt	1.67
C	1.64

Table 4. Values of pH, C, and N in the Breton profile.

Horizon	pH	% C	% N	C/N
L	6.1	35.5	1.47	24
F	5.6	35.0	1.56	22
H	4.9	20.3	0.83	24
Aeh	4.7	2.3	0.05	46
Ae1	4.9	0.4	0.06	7
Ae2	5.1	0.2	0.04	5
AB	5.2	0.2	0.03	7
Bt1	5.2	0.4	0.05	8
Bt2	5.1	0.4	0.05	8
Bt3	4.8	0.4	0.04	10
BC1	4.9	0.2	0.04	5
BC2	4.9	0.2	0.03	7
BC3	4.8	0.2	0.04	5

Table 5. Cation exchange capacity and exchangeable cations of the Breton profile.

	Exchangeable Cations (expressed as % of total exchange capacity)					Total Exchange Capacity (Σ)	Total Exchange Capacity (det'd)
Horizon	Na	K	Ca	Mg	Exchange Acidity	meq/100g	meq/100g
Aeh	0.3	12.0	73.0	20.0	45.0	9.4	14.3
Ae1	0.4	10.5	74.0	15.1	38.7	7.0	9.2
Ae2	0.4	5.1	74.3	20.2	29.6	5.0	6.3
AB	0.2	4.5	71.6	23.7	15.2	9.9	10.7
Bt1	0.2	2.8	70.8	26.3	10.0	20.0	18.6
Bt2	0.1	2.1	71.3	26.3	12.0	27.5	22.7
Bt3	0.4	1.2	69.2	29.2	10.7	21.5	20.5
BC1	0.3	1.7	68.2	30.0	10.5	20.9	19.7
BC2	0.5	1.2	67.9	30.4	10.8	19.5	20.1
BC3	0.4	0.7	68.2	30.6	11.2	21.5	18.4

Table 6. Pyrophosphate and dithionite-citrate-bicarbonate extractable Fe and Al (% of oven-dry weight).

	Dithionite-Citrate -Bicarbonate		Pyrophosphate	
	Fe	Al	Fe	Al
Aeh	0.44	0.35	0.37	0.07
Ae1	0.48	0.20	0.23	0.06
Ae2	0.44	0.15	0.10	0.03
AB	0.43	0.15	0.21	0.04
Bt1	0.44	0.50	0.34	0.22
Bt2	0.67	0.40	0.21	0.10
Bt3	0.73	0.38	0.27	0.10
BC1	0.75	0.35	0.34	0.15
BC2	0.71	0.00	0.18	0.04
BC3	0.71	0.38	0.17	0.04

pyrophosphate extractable Fe and Al in the Bt and upper BC horizons. This is thought to be a result of the movement of organically complexed weathering products from the upper horizons into the lower horizons. This finding supports the hypothesis of Douchaufour (1971) that lessivage involves the movement of amorphous Fe as well as colloidal clay. There is an increase of dithionite-citrate-bicarbonate extractable Al in the Bt1 horizon compared to the A and lower Bt horizons. It may be that finely divided hematite and geothite, and oxides of Fe and Al are also mobile in the process of lessivage.

The profile under study differs from the Breton soil series in that it is very deeply leached. Lime is not found within the solum nor is it found at 2.5 m. The lower horizons were classified in the field as being C horizons, however the deep leaching as indicated in the lack of lime at 2.5 m and the presence of argillans (see Micromorphology section) at depth indicates these are BC horizons and are transitional to the parent material. Values for pH remain moderately acid (4.9) to a depth of 2.5 m. The results for pH are very similar to those reported for the Breton series by Pawluk (1961); and Lindsay et al. (1968). The soil is slightly to moderately acid in the Ae horizon and becomes somewhat less acidic in the Bt. Total exchange acidity is much greater in the surface organic litter horizons than in underlying mineral horizons. A slight increase in exchange acidity is noted in the Bt horizon.

MINERALOGY

Analysis of the mineralogical characteristics of the soil profile reveals specific information about the pedological changes that have occurred over time. Of special interest to the study of Luvisolic soils is the translocation of clay and mineral weathering.

CLAY MINERALOGY

The mineralogy of the total clay sized fraction is reported in Table 7. Surface area, cation exchange capacity, loss on ignition, and elemental analysis of the coarse and fine clay fractions are presented in Tables 8, 9, 10, and 11. Appendix A contains typical X-ray diffraction patterns of the total and fine clay sized fractions from the Ae, Bt and BC horizons.

These data indicate that the Breton soil contains a uniform suite of clay minerals. The proportion of each mineral species is somewhat variable throughout the profile. The mineral suite is composed of smectite, mica, and vermiculite-like minerals. Small amounts of quartz, chlorite, and amorphous compounds are also present.

Soil vermiculite is thought to be depotassified mica. The X-ray diffraction characteristics of soil vermiculite differ from true vermiculite in that collapse of the crystal structure to a 10 Å (001) spacing occurs following K treatment and rehydration does not occur at 54% RH. This mineral exhibits expansion beyond 14 Å on treatment with ethylene glycol unlike geological specimens of vermiculite. These X-ray diffraction characteristics

Table 7. Semi-quantative mineralogy of the total clay fraction of the Breton profile from X-ray diffraction analysis.

Horizon	Mica	Hydrous Mica	Smectite	Soil Vermiculite	Chlorite	Amorphous Compounds	Quartz
Aeh	Mj	-	Tr	Mj	Tr	Mj	-
Ae1	Mj	-	Mj	Mj	Mn	Mn	Tr
Ae2	Mj	-	Mn	Mj	Mn	Mn	Tr
AB	Mj	-	Mj	Mn	Tr	Tr	-
Bt1	Mj	-	Mj	Mn	-	Tr	-
Bt2	Mj	Tr	Do	Mn	-	Tr	-
Bt3	Mj	Tr	Do	Mn	-	Tr	-
BC1	Mj	Tr	Do	Mn	-	Tr	-
BC2	Mj	-	Do	Mn	-	Tr	-
BC3	Mj	-	Do	Mn	-	Tr	-

Do = dominant > 50%
Mj = major 10 - 50%
Mn = minor 1 - 10%
Tr = trace

Table 8. Weight loss on ignition and chemical analysis of the coarse clay fraction (expressed as % of oven-dry weight).

Horizon	Loss on Ignition	K_2O	MgO	Al_2O_3	Fe_2O_3
Aeh	10.3	1.1	0.8	11.6	4.8
Ae1	6.3	0.8	0.4	5.1	2.1
Ae2	7.5	2.2	1.1	10.5	4.3
AB	6.1	2.2	1.0	9.1	3.7
Bt1	7.1	1.8	1.2	9.4	4.2
Bt2	8.0	2.0	1.9	9.7	4.4
Bt3	8.0	1.9	1.7	9.6	4.4
BC1	8.0	2.0	1.8	9.1	4.5
BC2	8.2	1.7	1.8	9.1	4.6
BC3	8.7	1.8	2.1	9.1	4.7

Table 9. Weight loss on ignition and elemental analysis of the fine clay fraction (expressed as % of oven-dry weight).

Horizon	Loss on Ignition	K_2O	MgO	Al_2O_3	Fe_2O_3
Aeh	14.2	2.2	2.3	32.5	19.6
Ae1	14.2	1.5	1.0	17.7	5.9
Ae2	14.7	0.5	0.4	5.7	2.7
AB	13.1	0.7	1.3	10.8	5.6
Bt1	12.6	1.1	1.5	11.2	6.9
Bt2	12.7	0.8	1.9	10.8	5.4
Bt3	12.3	0.7	1.8	11.9	6.0
BC1	12.6	0.9	2.4	14.2	7.3
BC2	12.4	1.0	1.6	7.1	7.0
BC3	9.0	1.2	1.9	14.8	7.9

are a result of strong hydrogen bonding and low charge density (Brown 1961). It is not possible to distinguish this mineral from beidellite without analyzing the a and b axis spacings. For the purpose of this thesis the term soil vermiculite will be used to describe the mineral exhibiting the aforementioned characteristics. Soil vermiculite is a major mineral in the A horizons. This is undoubtedly a result of a more intense weathering regime in the upper solum.

Mica is a major mineral throughout the soil solum. The content of mica throughout the profile is less variable than the content of the other clay mineral species. It is apparent from X-ray diffraction and chemical analyses that mica is more abundant in the coarse clay fraction than in the fine clay fraction. Values of mica content in the coarse clay fraction are generally in the 19 - 25% range, while in the fine clay fraction values are generally in the 8 - 15% range. There appears to be a slight bulge in the content of the mica in the fine clay fraction from the Bt1 horizon compared to the Ae horizons and lower B horizons. A slight bulge in the content of mica also occurs in the coarse clay fraction of the AB horizon. The high content of mica in the fine clay fraction of the Aeh and Ae horizons is attributed to negative enrichment of mica due to the removal of smectite as will be discussed shortly. The low content of mica in the coarse clay fraction in the Aeh and Ae1 horizon may be attributed to weathering. A higher content of coarse mica in the Ae2 and B horizons suggests that the weathering regime is less intense than in the Ae1 horizon.

The results indicate that fine clay size smectite has been depleted from the Ae horizons and has accumulated in the Bt horizons. X-ray diffraction analysis revealed that smectite is the dominant clay mineral in the fine clay fraction, mica is present as a major component, and soil vermiculite is present in minor quantities. Surface area determinations, cation exchange capacity, and K content of the fine clay fraction fully support the X-ray diffraction analysis.

It can be conclusively stated that the increase in total clay and fine clay in the Bt horizon is a result of lessivage; fine clay size smectite being the mineral which has accumulated in the Bt horizon. This finding concurs with the theory of lessivage as described in Soil Taxonomy (1978) and by authors such as Duchaufour (1971); Bullock (1968); and Wang (1971).

Weight loss on ignition to 850°C is attributed to the dehydroxylation of clays and amorphous compounds and to the oxidation of organic matter. Generally, the weight loss on ignition is greater for the fine clay fraction than for the coarse clay fraction. It is noted, that for the fine clay fraction there is a greater weight loss on ignition in the Ae horizons as compared to the B and C horizons. This is attributed to higher contents of amorphous mineral compounds in the fine clay fraction of the Ae horizons. This is an indicator that weathering is more intense in the A horizons compared to the B horizons. It is probable that the oxidation of organic matter is responsible for the larger weight loss in the coarse fraction of the Aeh horizon compared to the weight loss of the coarse clay fraction

Table 10. Surface area and cation exchange capacity of the fine and coarse clay fractions.

Horizon	Surface Area (m^2/g)		Cation Exchange Capacity (meq/100g)	
	2 - 0.2 μm	<0.2 μm	2 - 0.2 μm	<0.2 μm
Aeh	183	549	27.5	60.9
Ae1	169	503	19.6	43.6
Ae2	143	611	22.6	32.5
AB	178	692	21.6	61.8
Bt1	253	766	30.1	62.4
Bt2	361	700	40.0	76.4
Bt3	344	799	39.7	73.4
BC1	344	798	35.6	70.5
BC2	403	786	45.4	72.2
BC3	391	779	45.3	62.8

Table 11. Content of mica and expandible components of the coarse and fine clay fractions.

	2 - 0.2 μm		<0.2 μm	
	% Mica	% Expandible Component	% Mica	% Expandible Component
Aeh	13	17	25	52
Ae1	9	16	18	49
Ae2	27	12	6	60
AB	25	15	8	68
Bt1	22	23	13	76
Bt2	24	34	9	79
Bt3	23	32	8	79
BC1	24	22	11	78
BC2	19	38	13	76
BC3	22	37	15	77

of the Ae1 and Ae2 horizons.

There is a greater proportion of amorphous compounds in the fine clay sized fraction of the B horizons than in the coarse clay sized fraction of the same horizons as indicated by weight loss on ignition. It has been reported that iron is translocated with clay during lessivage (Duchaufour 1971). No doubt some of the amorphous mineral components in the fine clay fraction of the B horizon are weathering products which have been translocated to the B horizon. It was noted that a slight bulge in organic C and pyrophosphate extractable Fe and Al occurred in the Bt horizons. This will also contribute to the higher weight loss on ignition of the fine clay sized fraction.

Elemental analysis indicates that the Fe content of the fine clay fraction is in the 6 - 7% range whereas the Fe content of the coarse clay fraction is in the 3.5 - 4.5% range. The higher content of Fe in the fine clay fraction may be accounted for by the presence of an iron rich variety of smectite known as nontronite as opposed to the magnesium rich type known as montmorillonite. The presence of nontronite in Alberta till is reported by Pawluk and Bayrock (1969).

SAND MINERALOGY

The results of petrographic analysis of the light and heavy sand fractions are reported in Tables 12 and 13.

It is important to establish the uniformity of the parent geological material from which the soil has developed during the course of any pedogenic study. A number of methods have been

Table 12. Mineralogy of the light (S.G. < 2.75) sand fraction (% of total count).

Horizon	Quartz	Plagioclase	K-Spar	Mica	Crypocrystalline	Organic	Altered[1]	Total Count
Aeh	62	3	Tr	Tr	4	Tr	29	358
Ae_1	63	1	Tr	Tr	6	2	28	356
Ae_2	71	1	Tr	Tr	3	Tr	24	352
AB	70	1	Tr	Tr	Tr	Tr	26	386
Bt_1	61	2	Tr	Tr	5	Tr	31	362
Bt_2	56	2	Tr	Tr	3	Tr	38	383
Bt_3	51	3	Tr	Tr	4	Tr	39	362
BC_1	57	Tr	Tr	Tr	3	Tr	38	353
BC_2	56	1	Tr	Tr	8	2	33	363
BC_3	57	2	Tr	Tr	3	Tr	37	382

Altered[1] - Generally these are quartz or feldspar grains showing some degree of sericitization

Table 13. Mineralogy of the heavy (S.G. >2.75) sand fraction (% of total count).

Horizon	Pyroxene	Amphibole	Mica	Garnet	Hematite Limonite Iron	Opaques Magnetite	Zircon	Altered[1]	% of Total Sand	Total Count
Aeh	7	7	5	7	25	18	2	29	2.6	350
Ae_1	8	13	7	8	14	19	2	30	2.2	357
Ae_2	4	5	11	4	21	11	Tr	44	2.2	352
AB	6	8	5	5	16	11	2	47	2.4	364
Bt_1	6	11	6	7	24	8	Tr	38	2.1	345
Bt_2	3	5	10	5	15	13	Tr	49	2.2	350
Bt_3	8	9	4	6	19	8	Tr	45	1.5	352
BC_1	6	5	4	9	27	7	Tr	43	1.9	350
BC_2	4	10	12	5	25	10	Tr	34	1.9	514
BC_3	5	7	6	6	17	12	Tr	45	2.2	516

Altered[1] - Often these are sericitized grains of quartz or feldspar. They may also be grains showing a high degree of weathering, weathered sandstone or siltstone, and grains showing other types of alteration.

designed to determine the homogeneity of parent geological materials (Abder-Ruhman 1980). By nature, till is a heterogeneous mixture of sand, silt, clay, and coarse fragments, consequently it has been difficult to establish limits that define a lithological discontinuity in till. It was felt that for this study standard mineral counting techniques would be sufficient to elucidate any significant discontinuity in the soil solum.

Petrographic analysis of the sand fraction revealed no evidence of a lithological discontinuity in the soil profile. Variations in the content of each mineral species throughout the profile is attributed to parent material variability. Twardy (1969) discusses the mineralogical variability of Alberta tills.

MICROMORPHOLOGY

A detailed micromorphological description of the profile may be found in Appendix B. The following is a summary of the important findings of the micromorphological analysis.

Isoband fabric, as described by Dumanski and St. Arnaud (1966), is noted in the Ae horizon. Isolated iron nodules are common in the Ae horizon; they are indicators of weathering and also of periodic reducing conditions.

Argillans occupy more than 1% of the area of slides from the Bt horizon, thus satisfying the requirement for a textural B horizon as defined in the Canadian System of Soil Classification (CSSC 1978). The thickness and number of argillans increase with depth. In fact argillans are most common and thickest in the deepest portion of the profile. This suggests that the zone of

greatest illuviation is in the BC horizons at depths of 1.5 m to 2 m.

The location of maximum argillan concentration at the base of the profile is somewhat incompatable with the observed maximum clay content which occurs in the Bt horizons. There are two possible explanations for this anomaly.

Bullock (1968) suggests that the clay bulge in a Bt may result partially from weathering in the upper profile. In this profile lithoclasts of siltstone and sandstone are much less common in the Bt horizon than in the BC horizons. Weathering of these has undoubtedly contributed to the increase in clay content of the Bt horizon.

Another explanation holds that active pedoturbation resulting from wetting-drying and freezing-thawing cycles is responsible for the disruption of the soil fabric in the upper solum. Void argillans in the upper horizons are destroyed and incorporated into the soil matrix due to these forces. Consequently argillans are less common in the upper solum than in the lower solum. Areas of clay concentration in the soil matrix provide micromorphological support for this argument. These clay concentrations may be interpreted as argillans in an intermediate state of mixing. Kremner (1969) discusses the opening and closing of cracks and pores in the soil as channels for clay migration. The opening and closing of cracks is a mechanism for mixing in the solum. Pawluk and Dudas (1978) discuss the reorganization of void argillans resulting from biological activity or physical processes in genesis of acid

Luvisols.

Bullock (1968) notes the presence of argillans at a depth of 2.3 m in the Langford soil. In the Breton soil argillans are also present at a depth of 2.5 m. This suggests, as noted by Bullock, that some clay may have been entirely removed from the solum. Argillans are most common in larger noncapillary vughs pores and channels indicating that illuviation is a result of suspensions of clay and water passing through noncapillary voids.

The lack of a lime layer and the presence of argillans indicate that flocculating cations are not necessary for the formation of argillans. This agrees with the work of Brewer and Haldane (1957) who showed that the orientation of argillans is enhanced if soluble salts are not excessive in the profile. Their work also suggests that clay orientation is a result of drying. This is likely the case at the Breton site as there are no soluble salts in the lower horizon to halt clay movement.

Gombeer and D'Hoore (1971) discuss the relative mobility of clay and induced clay migration. They note that as dilute suspensions of clay-water flow towards layers of higher matric suction, water is lost. Thus during movement the soil/water ratio is increased and approaches an incipient flocculation ratio. It is at this point of flocculation that argillan formation must occur. In essence there is capillary withdrawal of water causing clay deposition as suggested in Soil Taxonomy (1978).

The lack of salts in the lower horizon does not indicate that $CaCO_3$ never plays a role in the genesis of the textural B

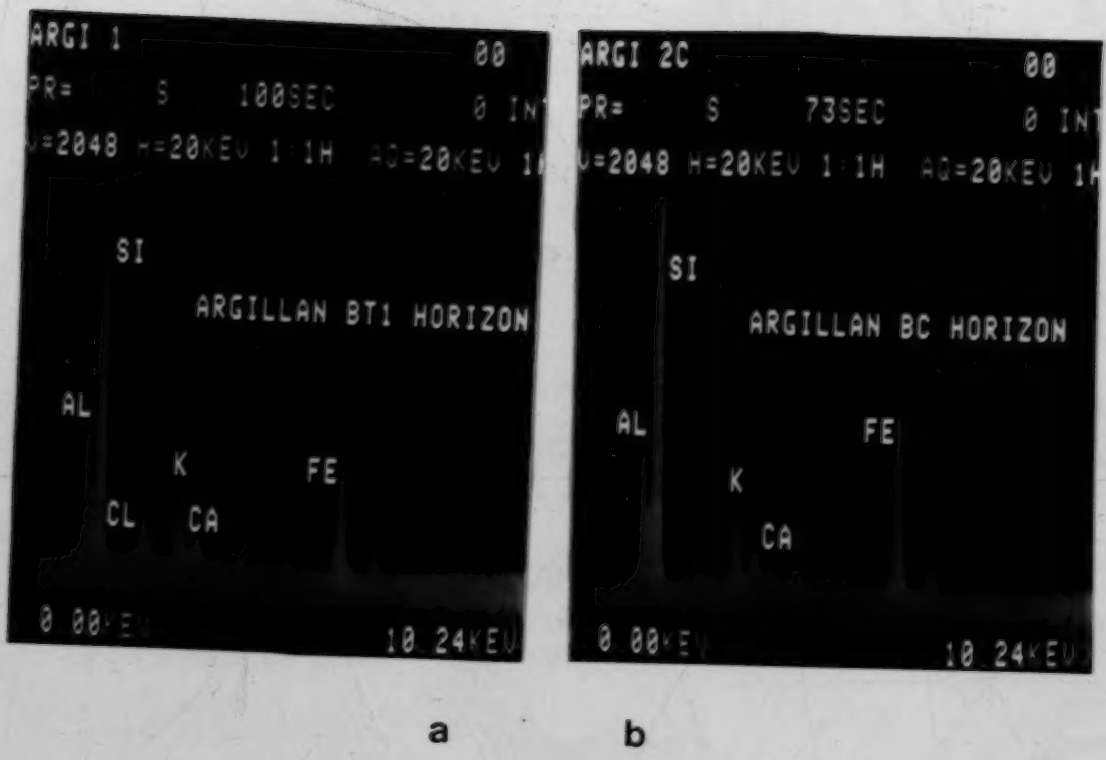
horizon. The presence of carbonates in the early stages of genesis may have been responsible for initial clay illuviation in the solum. Argillans in the Bt horizon are not as well oriented nor as thick as those in the lower horizons. This may result from the presence of a flocculating cation in the lower horizon at the time of deposition.

It is apparent from micromorphological examination that sieving as a mechanism for illuviation of clay is inoperative in the Breton soil. Throughout the profile, argillans are found along the walls of vughs and pores hundreds of times larger than clay particles themselves. The presence of argillans in the cracks and pores suggests that sieving does not occur in that clays that have been sieved would not be oriented but would be lodged at irregular angles to one another. Subsequent pedogenic activity would not erase evidence of lodging. This negates the possibility of sieving and adds weight to the argument that argillans are a result of drying.

The presence of silt particles in the matrix of argillans, as shown in Figure 3, is reasonably common in the solum. They may result from silt moving with the clay or they may also be derived from the matrix close to the argillans in question. Brewer (1964) indicates that stress argillans are characterized by the presence of silt particles derived from the soil matrix.

Argillans in the upper B exhibit different optical properties when compared to argillans from the lower B. They show "mica type" extinction and less strong orientation. Energy dispersive analysis (Figure 4) indicates that K is twice as abundant in

Figure 3. Photograph of silt sized quartz grains in the matrix of an argillan (crossed polarizers). 32X



a b

Figure 4. Energy dispersive patterns from argillans in a) the upper Bt horizon, and b) the lower Bt horizon.

argillans from the upper B horizon. This indicates that argillans in the upper B contain more mica than those in the lower B. An explanation of this situation is discussed in the section on dynamic pedology.

DYNAMIC PEDOLOGY

Singer (1978) describes dynamic pedology as an attempt to monitor soil forming processes as they occur in situ. This is contrasted to the static approach where pedogenesis is inferred from examination of the pedon with the assumption that the pedogenic processes have proceeded uninterrupted over time and that they are continuing today. In a number of studies, (Singer et al. 1978; Dawson et al. 1979; Ugolini et al. 1977ab), tension lysimeters have been used to study the process of podzolization in situ, as it is occurring today. This study has made use of gravity lysimeters, canopy drip collectors, and soil temperature-moisture monitoring equipment to study the process of lessivage.

Soil Moisture-Temperature Regimes

Soil moisture and temperature were monitored on a weekly basis from spring to fall in the years 1977 and 1978. The data for soil temperature are presented as a monthly average at selected depths in Figures 5 - 8 and in Appendix D.

Temperature in the soil shows a very definite and predictable trend from spring to fall. In April of 1978 the profile was more or less isothermal with temperatures close to freezing. In May of both years a warming trend is noted through

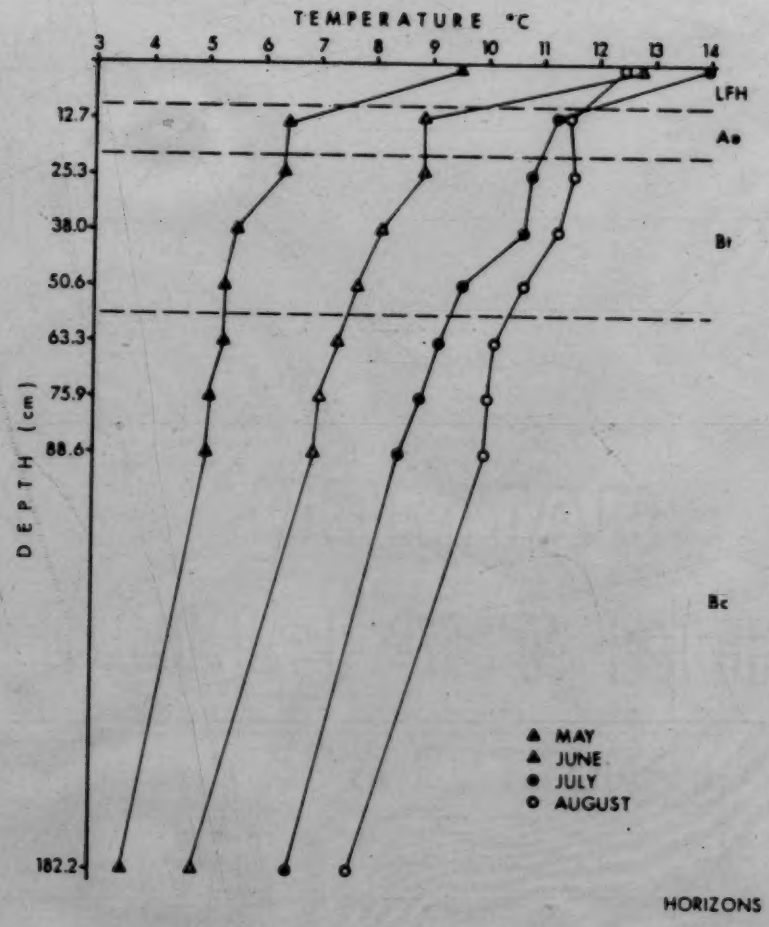


Figure 5. Graph of soil temperature versus depth from May to August, 1977.

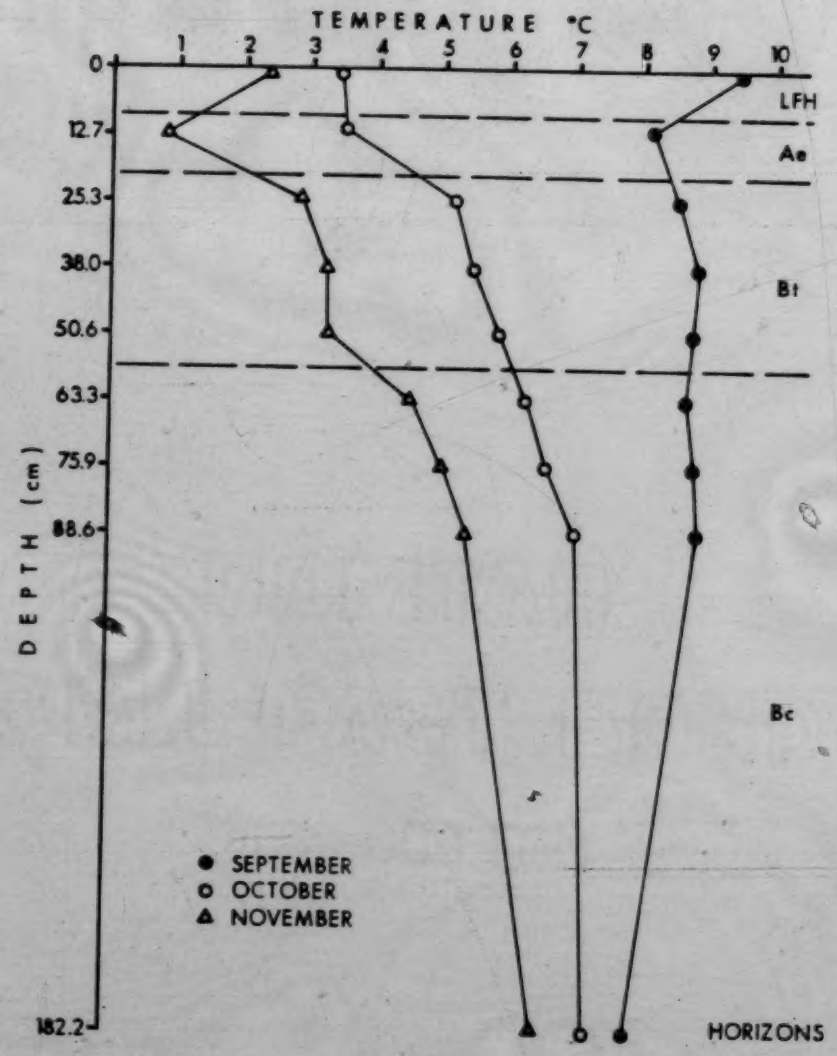


Figure 6. Graph of soil temperature versus depth for September to November, 1977.

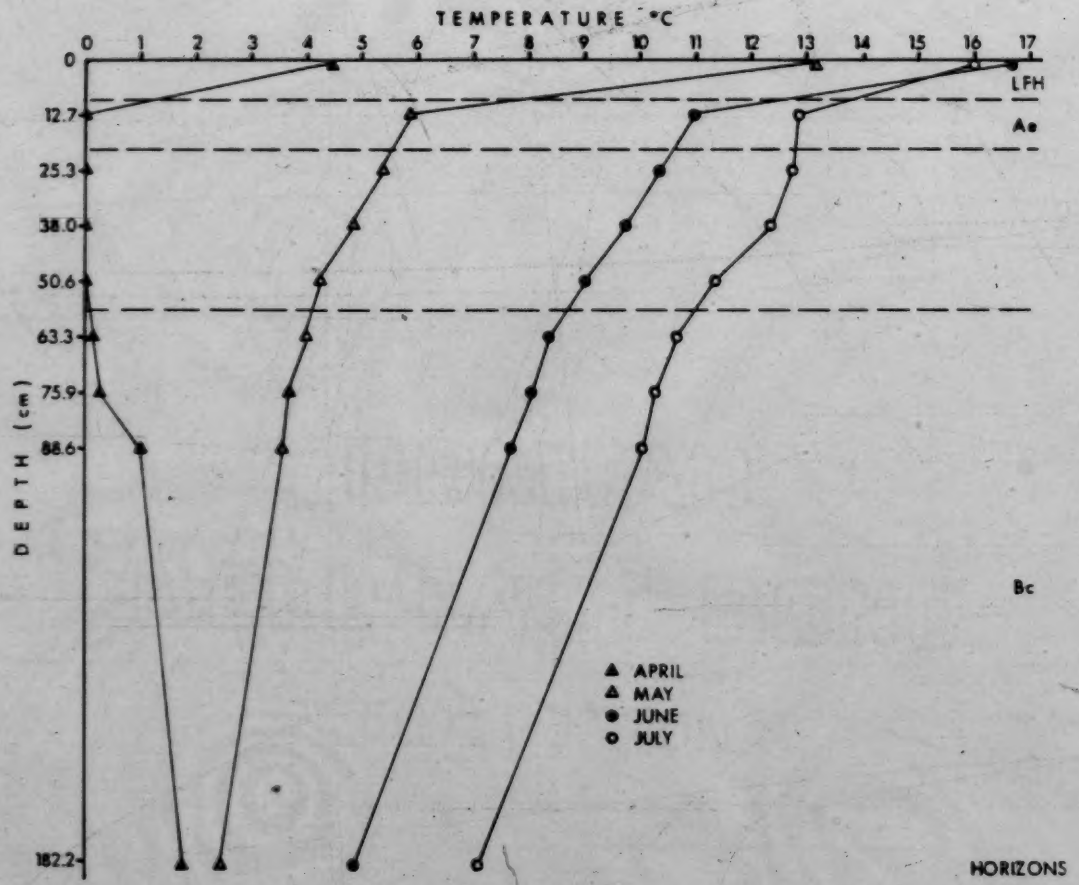


Figure 7. Graph of soil temperature versus depth for April to August, 1978.

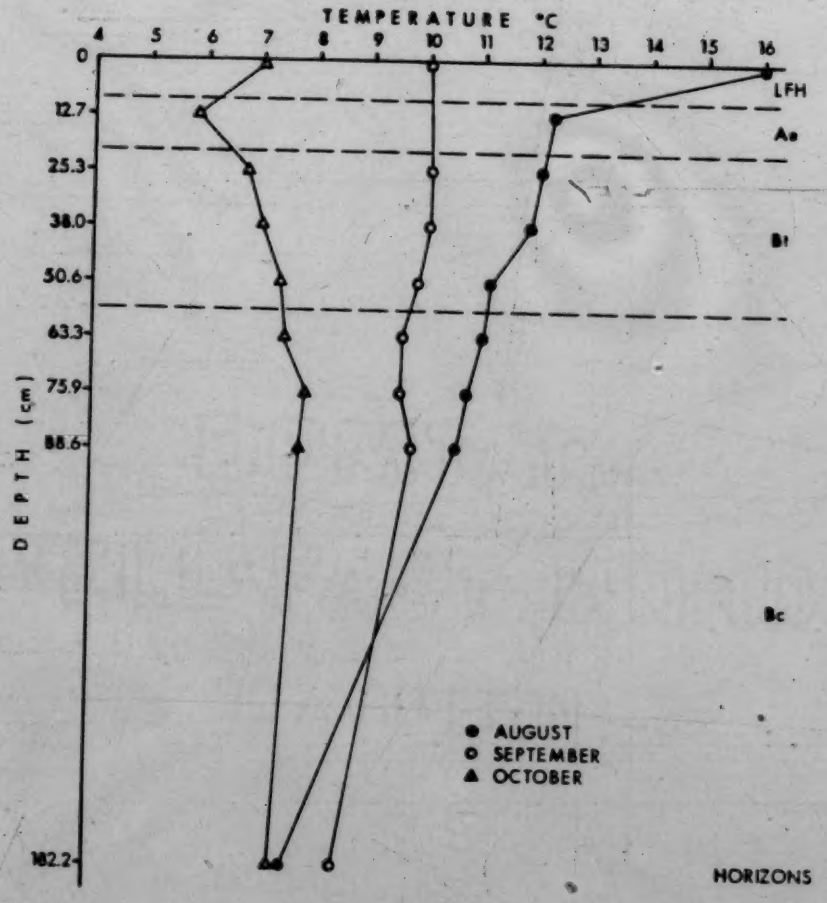


Figure 8. Graph of soil temperature versus depth for September to November, 1978.

the whole profile. This trend continues until August, after which cooling throughout the profile occurs. This cooling trend continues throughout fall and winter; the amount of heat loss being proportional to such factors as seasonal air temperatures, the thickness of snow cover and the amount of water in the profile. Periodic examination of soil temperatures over the winter indicated that temperatures remained close to freezing (0°C) under snow cover. The curve of soil temperature for April 1978 supports this.

The fluctuation of soil temperature from spring to fall is greatest in the upper (10 cm) of the solum. Below this depth changes in temperature are less marked. Over the 1978 season the average daytime soil temperature at 180 cm changed 6°C while the surface soil temperature changed by twice that amount (12°C).

This temperature fluctuation in the upper solum plays a significant role in weathering reactions and in biological transformations. The results of monitoring soil temperature suggest that this soil has a mean annual temperature of 8°C or less. This corresponds to values set for Luvisolic soils in the Canadian System of Soil Classification (CSSC 1978).

Monthly records of soil moisture and precipitation for 1977 and 1978 are shown in Figures 9 and 10 and in Appendix D. The results for 1977 clearly show a seasonal moisture deficit in the fall of the year. Rainfall drops off significantly in September and through the months of September, October, and November, the moisture content in the LFH, and Bt horizons exhibits a

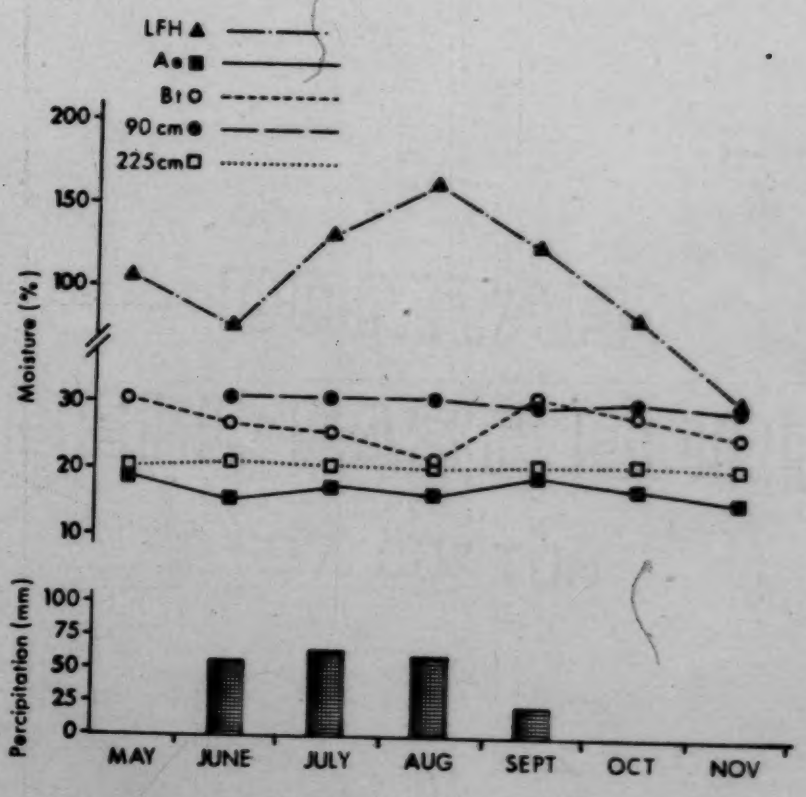


Figure 9. Mean monthly soil moisture contents and precipitation for 1977.

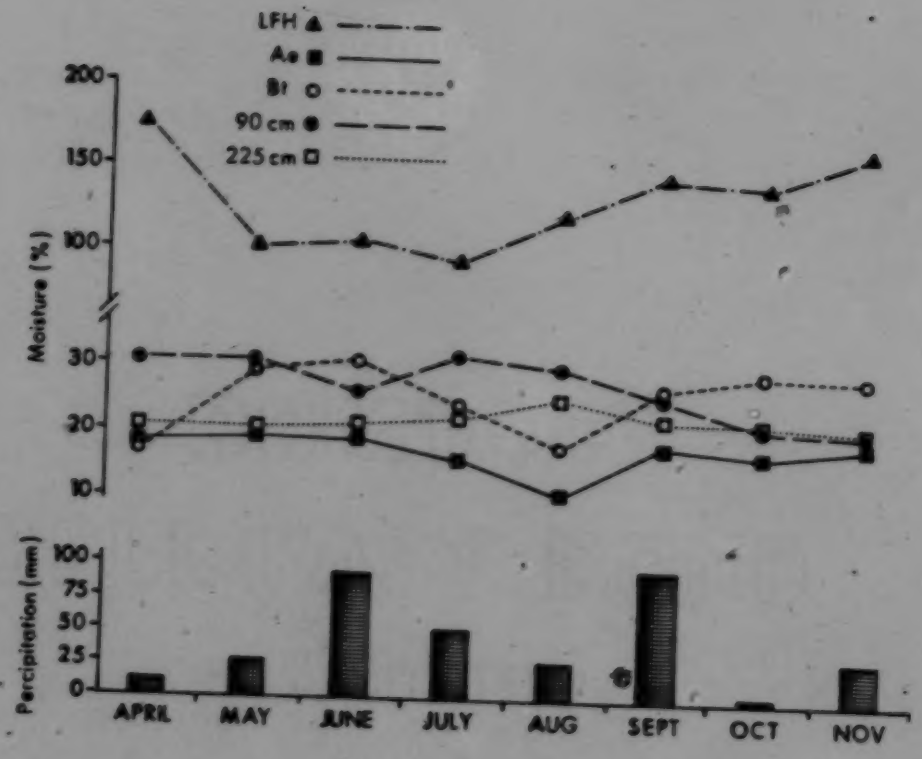


Figure 10. Mean monthly soil moisture contents and precipitation for 1978.

concomitant loss of moisture. This illustrates that the seasonal moisture deficits as specified in Soil Taxonomy (USDA 1978) do occur and that a climatic moisture deficit induces a soil moisture deficit.

Precipitation in 1978 is somewhat anomalous compared to the expected pattern. Normally the amount of precipitation drops off during the growing season and very little rain is expected in the months of September through November. Precipitation drops off markedly in July and August of 1978 compared to June, creating a soil moisture deficit in the Ae and Bt horizons. Moisture content would be expected to drop off even further in September, however there were heavy rains in that month totalling 98 mm. As a consequence of this rain the soil moisture increased marginally in the fall of the year.

It is obvious from Figures 9 and 10 that there is little variation in soil moisture in the lower soil horizons through the year. At 90 cm the soil remains close to 30% moisture and at 2.25 m the moisture content is somewhat more variable ranging from 20 - 27%. The 1/3 bar moisture content of the C horizon of the soil at the Breton plots is reported to be 26.3% (Dr. J. A. Robertson, personal communication). The moisture content at 90 cm was somewhat greater than this over the two year study period whereas the moisture content at 2.25 m is somewhat lower than the 1/3 bar moisture content.

In contrast the LFH, Ae and Bt horizons show very marked fluctuations of moisture content. The LFH horizon contains the greatest amount of water and undergoes the greatest change in

moisture over the season. The Ae and Bt horizons have less marked changes in moisture content over the season and exhibit a delayed response to rainfall. The Ae horizon is coarser in texture and is observed to contain much less water, on a seasonal basis, than the LFH or Bt horizons. Monthly fluctuations in moisture content within the Ae horizon are also small compared with changes in moisture content of the Bt horizon. These observations suggest that excess water moves rapidly through the Ae either laterally or vertically.

Heapy (1971) reports the 1/3 bar moisture content of the upper 15 cm of two Breton profiles to be slightly over 18% and the 15 bar moisture content to be between 6 and 7%. The moisture content of the Ae horizon during the two year study period fluctuated from slightly above 18% to 11% with the majority of readings between 15 and 18%. This suggests that temporary reduction may occur in the Ae horizon and that this may be responsible for the mobilization of Fe as suggested by Duchaufour (1978). This also suggests that water and clay are moving through noncapillary voids in the Ae horizon.

Figures 11 and 12 depicting the weekly variation of soil moisture in the LFH, Ae, and Bt horizons clearly show the response in each horizon to precipitation events and to periods without rainfall. The LFH horizon responds in an immediate and pronounced fashion to rainfall events. Even fairly light rainfall causes the moisture content to increase by several percent. The length of time that excess moisture remains in the LFH horizon at least in part is a function of plant uptake, evaporation, and

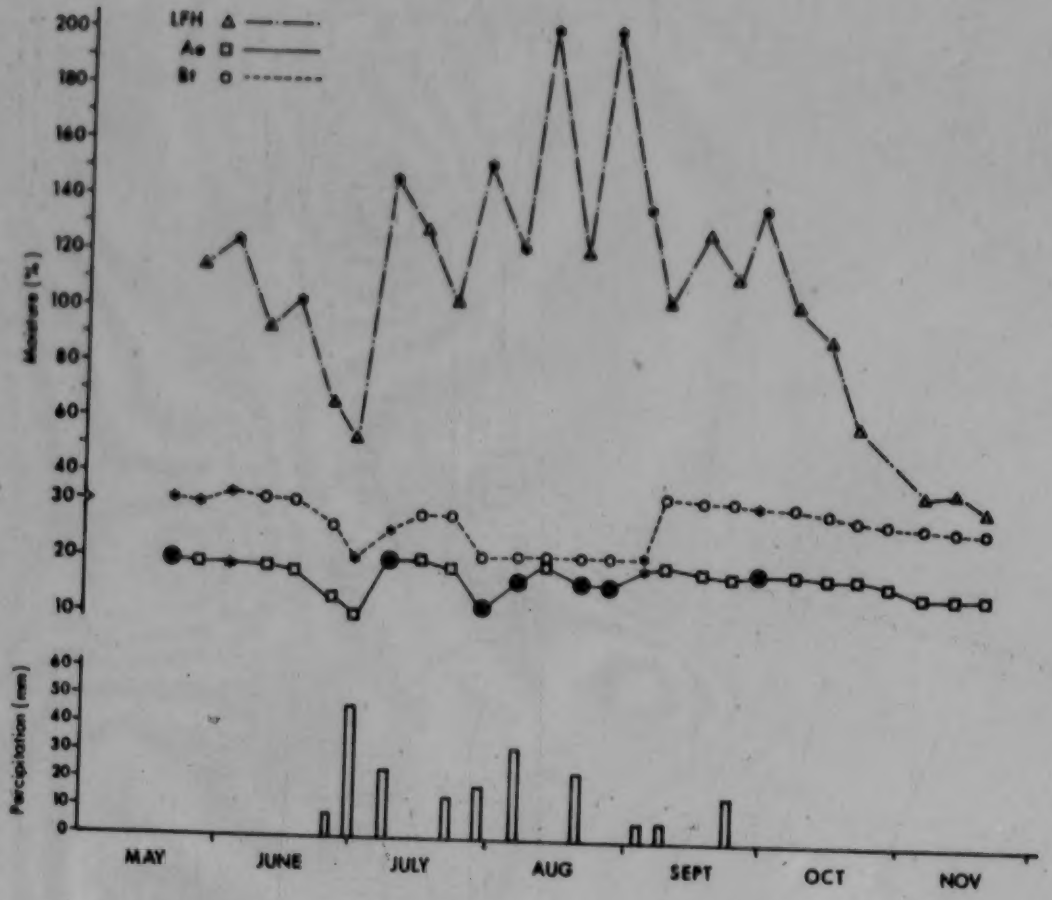


Figure 11. Weekly values of soil moisture content and precipitation for 1977.

● Dates upon which leachate samples contained colloidal material.

* Dates upon which leachate samples were collected.

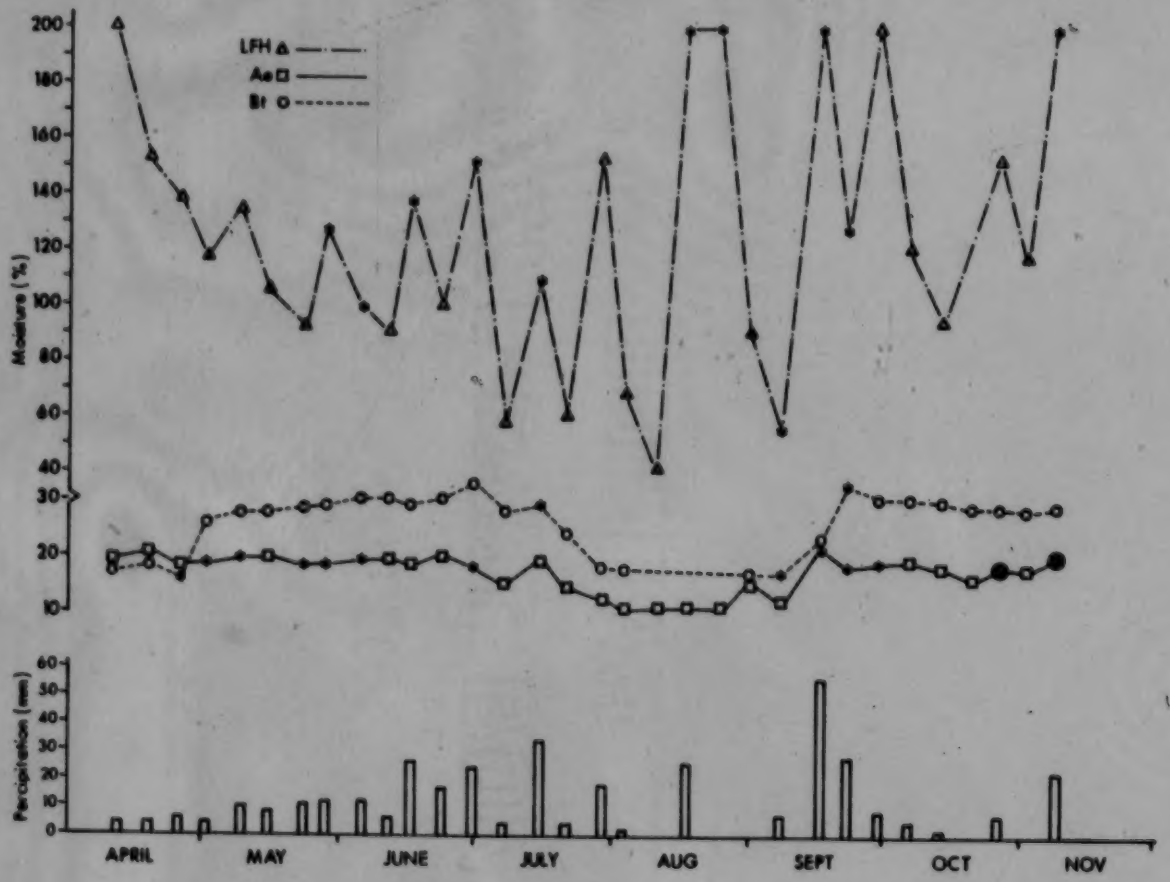


Figure 12. Weekly values of soil moisture content and precipitation for 1978.

● Dates upon which leachate samples contained colloidal material.

* Dates upon which leachate samples were collected.

the matric suction exerted by the lower soil horizons.

The moisture content of the Ae horizon is much lower than the LFH. This is expected, given the coarse texture and low organic matter content of the Ae horizon. The Ae responds less markedly than the LFH to rainfall events. In 1978 the moisture in the Ae horizon remained constant from May to June even though a number of significant rainfalls occurred. In August of that year the amount of rainfall dropped substantially; a concomitant loss of moisture from the Ae horizon was noted. Rainfall during August increased the moisture in the LFH horizon but not in the Ae horizon. This suggests that the LFH although very wet, did not allow water to move downward into the rest of the soil profile. More than likely plant uptake of water contributed to this infiltration blockage. Matric suction of the Ae and Bt horizons obviously has little effect on moisture movement from the LFH horizon.

The Bt horizon contains more moisture than the Ae horizon (a function of texture) and exhibits a different response to precipitation. A period of drying occurred in August 1978 followed by an increase in moisture following a very heavy rain in September. The moisture response of the Bt is marked and immediate, indicating that the Ae horizon is very efficient in passing rain waters to the Bt horizon. The increased moisture content is sustained for the remainder of the season in the Bt horizon.

The Ae and Bt horizons appear to be particularly susceptible to moisture deficits. In August of 1978 the moisture

content of each dropped markedly when rainfall was low. This drop was likely due not only to evaporation but also to the removal of water by plants which require moisture during warm weather.

Examination of the profile in winter (1977/78) indicated that while the LFH and Ae horizons were frozen solid the AB and Bt horizons remained non-cohesive and moderately friable. Temperatures were below freezing in these latter horizons but there was insufficient moisture present for freezing to cause cohesion of soil particles. Careful study of the Ae horizon with the naked eye and field microscope showed lenses of ice in the platy structure. These lenses were clearly reinforcing the structure of the horizon by forming between individual plates and causing some compression of individual units.

The presence of ice lenses in the Ae horizon was unexpected. Figure 11 of weekly soil moisture readings for 1977 indicates that both the LFH and Ae horizons were quite dry in the late fall. Certainly there was no free water in the Ae that could form these lenses. The lenses may be a result of early snowfall that melted and infiltrated into the soil. It might also be speculated that water vapour had moved from lower horizons into the Ae in response to a temperature gradient created by a frozen surface. There is no evidence to support either theory as weekly monitoring of the site was discontinued in the late fall.

The groundwater well was monitored regularly. In the spring of each year the water table was present at considerable depth and fell below the 4.2 m depth of the well early in the

season. These observations lead to the conclusion that groundwater does not play a significant role in the genesis of the Breton soil. However, observations at the site were continued into 1980 and throughout that year the water table was within 4.2 m of the surface. In 1980 a significant amount of precipitation fell during the growing season and caused the rise in groundwater. Although the water table was well below the soil solum it is apparent that in some years groundwater may have an influence on the soil solum. This may be the explanation for the faint mottling in the lower portion of the solum.

Leachate Collection

Leachates were collected from each of the three lysimeters whenever solution was present in the collection container. Samples were often small (volumetrically) and it was necessary on occasion to combine several collections in order to perform a complete analysis on a given sample. In particular, samples from the Bt horizon rarely had volumes greater than 10 ml. The greatest number of samples came from the LFH and Ae horizons. Those from the Ae lysimeter often contained colloidal material which could be separated by centrifugation. Samples from the Bt lysimeter were, with only one exception, clear. The dates on which samples were collected from the lysimeters are recorded in Figures 11 and 12.

In 1977 colloidal material was found in suspension in the Ae sample on seven occasions. In 1978 there was very little solid material collected during the season. It was not until late in

the fall of that year, that a flush of water containing a large quantity (0.25g) of colloidal material moved into the Ae lysimeter. This comprised 95% of the solid material collected for the year.

In May of 1979 a large volume of water containing a trace of colloidal material was collected from the Bt lysimeter. This was the first and only time in the two year study period that colloidal material was collected from the Bt lysimeter.

The implication of these observations is that clay migration in Luvisolic soils is not necessarily a gradual continuous action. In fact, a flush or concentration of colloidal material may move rapidly from the Ae to lower horizons in response to heavy sustained rainfall as seen in 1977. Clay migration may also occur in a continuous fashion over a period of time. Although solutions containing colloidal material were collected as they left the Ae horizon, samples with colloidal material were not present in the Bt horizon lysimeter. This is further evidence that although the clay may move in small increments, these do not penetrate to any depth in the Bt horizon. A heavy rainfall following a dry period is required for deep penetration of leaching solutions into the profile. There also appears to be a lag period between rainfall events and the movement of water into the lysimeters. This makes it very difficult to correlate rainfall events with colloidal material collection.

Canopy Drip Analysis

The results of the analyses performed on canopy drip

samples are found in Tables 14 - 17. Of the cations in canopy drip samples, K is the most abundant. It shows the greatest variation in concentration ranging from 2 mg/1 to 35 mg/1. Ca and Na are less abundant in these samples and show much less variation. Mg is the least abundant cation in canopy drip samples. Values for Mg are 1 mg/1 or less.

There appear to be no differences in cation concentrations between poplar and spruce canopy drip samples. Values of pH are nearly neutral for samples from both species. Spruce canopy drip tends to be slightly more acidic than that under poplar. Values of pH for canopy drip samples in 1977 tend to be lower than those in 1978.

In general, pH values are less acidic than expected given the results of other researchers (Parker 1978; Mahendrappa 1974). This difference may be explained in two ways. Firstly, in the case of aspen, Parker (1978) suggests that the presence of bicarbonate as a major anion in aspen throughfall may be responsible for pH values greater than 5.0. With the concentration of K in these solutions, the hydrolysis of $KHCO_3$ would cause high pH values. In some months pH values are greater than 8; these values are close to those expected in solutions containing $KHCO_3$. Unfortunately, neither this study nor that of Parker tested for bicarbonate, thus its effect on pH values cannot be substantiated. Secondly, the measure of pH values cannot be accepted unequivocably as samples may have remained in the canopy drip collector for periods as long as seven days. Equilibration of the samples with the atmosphere can

Table 14. Mean monthly concentration (mg/1) of cations and pH of aspen canopy drip 1977.

	May	June	July	Aug	Sept	Oct	Nov	$\bar{x}$	s
K	2.2	16.4	3.5	2.2	15.7	-	-	8.0	7.3
Na	0.8	2.8	0.2	0.2	0.3	-	-	0.8	1.1
Ca	1.1	2.1	1.1	1.0	5.3	-	-	2.1	1.8
Mg	0.3	0.9	0.3	0.2	1.3	-	-	0.6	0.5
pH	7.0	6.6	6.7	6.3	7.2	-	-	-	-

Table 15. Mean monthly concentration (mg/1) of cations and pH of spruce canopy drip 1977.

	May	June	July	Aug	Sept	Oct	Nov	$\bar{x}$	s
K	3.6	8.4	18.1	11.0	3.3	-	-	8.9	6.1
Na	0.5	1.7	0.4	0.5	2.3	-	-	1.1	0.9
Ca	1.2	1.8	3.0	1.4	3.4	-	-	2.2	1.0
Mg	0.3	0.7	0.7	0.4	1.4	-	-	0.7	0.4
pH	6.6	6.6	6.9	6.5	6.5	-	-	-	-

Table 16. Mean monthly concentration (mg/l) of cations, organic constituents and pH of aspen canopy drip 1978.

	April	May	June	July	Aug	Sept	Oct	Nov	$\bar{x}$	s
Polyphenols	-	26.1	39.6	3.6	2.7	3.8	1.6	1.0	9.8	14.0
Polyuronides	-	15.6	24.2	4.7	4.2	6.1	6.8	6.0	9.7	7.5
Carbohydrates	-	15.3	21.8	8.6	4.2	3.0	5.4	2.8	8.7	7.2
K	-	7.3	17.7	12.9	5.2	9.3	10.8	4.6	10.0	5.0
Na	-	3.8	2.9	6.2	4.0	4.3	2.2	2.5	3.7	1.3
Ca	-	3.3	3.6	2.3	2.3	3.1	3.2	3.4	3.1	0.7
Mg	-	0.5	1.2	1.2	0.5	0.9	1.0	0.5	0.8	0.3
pH	-	7.8	7.6	7.8	7.4	7.3	8.0	7.1	-	-

Table 17. Mean monthly concentration (mg/l) of cations, organic constituents and pH of spruce canopy drip 1978.

	April	May	June	July	Aug	Sept	Oct	Nov	$\bar{x}$	s
Polyphenols	-	23.1	28.3	9.0	5.0	8.0	3.1	-	12.7	10.3
Polyuronides	-	16.0	21.5	11.0	7.2	6.0	7.1	-	11.4	6.1
Carbohydrates	-	17.3	22.6	17.3	7.6	6.0	4.5	-	12.6	7.5
K	34.5	12.3	17.4	12.2	10.7	12.5	13.8	9.0	15.3	8.1
Na	2.9	3.0	4.0	4.1	4.2	3.8	2.2	2.0	3.3	0.9
Ca	20.1	4.1	3.6	3.3	2.2	2.5	3.8	4.0	5.5	5.9
Mg	8.5	1.1	0.9	0.5	0.5	0.3	1.3	1.0	1.8	2.7
pH	6.6	7.3	7.6	7.1	6.7	6.8	8.2	8.2	-	-

produce changes in pH. The magnitude of this change is proportional to temperature, CO_2 concentration in the air and the period of time for equilibration. That pH values are so close to or even greater than neutrality is significant. It has been generally accepted that Luvisols develop under acidic conditions as pH values of the soil are moderately acid. However, these results indicate that canopy drip and lysimeter leachates from the LFH horizon are not acidic. This leads to the conclusion that acidic conditions in the solum are a result of mineral hydrolysis.

The results for cation concentrations reported herein are in general agreement with those reported by Parker (1978). The concentration of cations in canopy drip decreases in the order K, Ca, Na, Mg. Parker reports that 70% of the K reaching the soil is the result of throughfall. K concentrations reported by Parker are somewhat lower than those found in this study. The reasons for any differences may be two-fold. Site factors such as the size, shape, and age of the canopy and the intensity and duration of rainfall strongly influence the concentrations of cations reaching the soil surface. A second point to consider is the effect of SO_2 emissions on K release from aspen poplar. Parker reports a significant increase in K concentration in throughfall at a site affected by SO_2 emissions. The Breton site is located in a gas field and small scale scrubbing plants are located in the area. It is possible that the local release of SO_2 may be affecting K concentrations in canopy drip.

The results for samples of canopy drip, appear similar to values for stemflow as reported by Mahendrappa (1974). In his

stemflow samples, the concentration of cations decreased in the order K, Ca, Na, Mg. He reported cation concentrations of stemflow under white spruce that are very similar to those of canopy drip reported in this study. The main difference is in Na concentrations. Na values in this study range from 2 - 6 mg/l and are virtually equivalent to those for Ca. Mahendrappa reports values of 0.9 mg/l for Na. This variability can be expected and may be the result of local factors such as Na content of rainfall or the uptake of Na from the soil solum. Parker (1978) reports that Na reaching the forest floor is derived from precipitation and not from vegetation.

The effects of the addition of cations in stemflow on soil properties have been discussed by Gersper and Holowaychuk (1970, 1971). These authors suggest that stemflow should be considered a factor of soil formation. The work of Parker (1978) indicates that although stemflow contains greater concentrations of nutrients than throughflow, sigificantly less stemflow reaches the soil surface. Thus canopy drip, although less concentrated, adds significantly greater quantities of nutrients to the soil.

The concentrations of organic constituents in the canopy drip samples are reported in Tables 16 and 17. These are not necessarily absolute values for concentration as these samples may have been in the collectors for periods up to seven days. During this time, some polymerization may have occurred or microbial activity may have modified the concentrations of soluble organic compounds.

The results indicate that in all cases the concentrations of

organic constituents in the canopy drip decrease substantially from Spring to Fall. This sharp drop in concentration may be the result of polymerization of organic constituents. It may be that the metabolic processes of plants change during the season so as to alter the volume of organic constituents produced. The duration and intensity of rainfall during this latter part of the season may also affect the amount of organic constituents found in canopy drip samples.

The values for polyphenol and polysaccharide content are quite low compared with those reported by Dormaar (1970). This may be due to polymerization of organic constituents. Dormaar took specific steps to prevent this reaction from occurring. The differences in concentration may also be due to the manner in which samples were collected. In this study, collectors were placed on the canopy floor to collect throughfall precipitation that had interacted with leaf surfaces. Dormaar, on the other hand, picked leaves and washed them in distilled water to simulate canopy drip. This method may have produced elevated evaluations of polyphenol and polysaccharide concentrations.

This study reveals that the concentration of polyphenols is greatest in spring when leaves are sprouting and seeds are developing while Dormaar's study indicated that it increased from spring to fall. This may be attributed to the area of leaf exposure and the intensity and duration of rainfall events or to the polymerization of organic compounds. Dormaar noted that as the season progressed simple phenolic compounds made way for more complex phenols. Polymerization or complexing could lead to

a significant decrease of "measureable" phenolic compounds entering the soil solum during summer and fall. It is probable that in nature polymerization of phenolic compounds from poplar and spruce leaves occurs quickly and results in a net decrease of phenols entering the soil in the later months of the growing season. Conversely, in the early part of the growing season, leaves are excreting simple phenols that enter the solum in much larger quantities, and have a greater potential to interact with soil materials than those excreted later in the season.

These results provide an estimate of the relative amounts of organic compounds and cations entering the soil body in canopy drip over the growing season. Lysimeters installed below the LFH, Ae, and Bt1 horizons collected samples of percolating water as it leached downwards. Changes in soil solution chemistry, the movement of colloidal leachates and the process of lessivage are all discussed in the following section.

Lysimeter Leachate Analysis

The concentration of organic constituents in solution leaching through the LFH horizon is somewhat lower than that found in canopy drip (Table 19). The samples collected from the LFH lysimeter were smaller than those collected in the canopy drip collectors. Consequently, it would be expected that the concentrations of the organic constituents would be greater in the lysimeter leachates than in the canopy drip samples. Since concentrations are lower in the leachates, it must be concluded that a net loss of organic constituents is occurring as water

Table 18. Mean monthly concentration (mg/l) of cations and pH of lysimeter samples collected from the LFH horizon 1977.

	April	May	June	July	Aug	Sept	Oct	Nov	$\bar{x}$	s
K	25.7	-	32.5	74.0	35.5	-	-	-	4.2	2.2
Na	5.4	-	6.3	4.0	4.7	-	-	-	5.1	1.0
Ca	10.9	-	10.8	11.8	12.1	-	-	-	1.1	0.6
Mg	3.2	-	2.9	3.1	2.8	-	-	-	3.0	0.2
pH	7.8	-	7.5	8.9	8.0	-	-	-	-	-

Table 19. Mean monthly concentration (mg/l) of major cations, organic constituents and pH of lysimeter leachates from the LFH horizon 1978.

	May	June	July	Aug	Sept	Oct	Nov	$\bar{x}$	s
Polyphenols	1.5	5.7	4.0	2.8	2.5	-	1.5	3.0	1.6
Polyuronides	12.0	7.3	16.0	10.8	5.0	-	8.0	9.8	3.9
Carbohydrates	11.0	7.3	9.0	7.3	5.8	-	8.0	8.1	1.8
K	14.8	29.0	29.0	24.2	19.8	-	20.0	2.3	5.6
Na	2.2	3.0	10.2	2.8	1.5	-	4.9	4.1	3.2
Ca	8.4	7.6	13.3	14.0	11.7	-	14.0	1.2	2.8
Mg	2.2	3.4	4.1	4.5	3.8	-	4.7	3.8	0.9
pH	7.4	7.3	7.5	7.1	8.2	-	7.6	-	-

leaches through the LFH horizon. This can be attributed to microbial activity, or polymerization reactions.

Changes in concentration of polyuronides and carbohydrates over the growing season follow a pattern very similar to the one noted in canopy drip samples. Greatest concentrations are present in the early months of the season and concentrations decline towards the fall. This pattern may be attributed to the amount of rainfall and to the chemistry of the canopy drip entering the soil solum. Concentrations of polyphenols in the LFH horizon lysimeter are low during the early months of the year and increase marginally towards fall. This is quite different from the pattern noted for canopy drip samples and for polyuronides and carbohydrates in lysimeter samples. It must be concluded that polyphenols reaching the soil surface in solution are removed from the leaching solution through polymerization or microbial attack. It is clear that these compounds are much more reactive in the soil than polyuronides or carbohydrates.

The concentration of all cations exiting the LFH horizon is greater than that of the canopy drip (Table 18 and 19). Again K is most abundant and shows the greatest variability in concentration. Ca is the second most abundant cation in LFH horizon leachates. Values for Na and Mg are also noted to be significantly greater in leachate samples than in canopy drip samples. This increase in cation concentration indicates that cation retention by the LFH horizon is probably not occurring. The increases in cation abundance may be attributed in part to concentration resulting from evapotranspiration.

The ratios K to Mg and K to Ca are lower for samples from the LFH lysimeter than for canopy drip samples. This suggests that a net loss of K is occurring or that a net increase of Ca and Mg is occurring in water leaching through the LFH horizon.

It is probable that the lower ratios are a result of both interactions. Undoubtedly, K is being removed from the soil solution by the growing vegetation. Additions of Ca and Mg are probably occurring as a result of the decomposition of organic matter in the LFH horizon. Parker (1978) reports that the order of return of nutrients to the soil under aspen is Ca, Mg, K followed by Na. This conclusion was based on total addition to the soil and included addition from litterfall, stemflow, and canopy drip. It is logical to assume that as decomposition of plant parts continues in the LFH horizon, Ca and Mg are added to the soil solution.

The results of analysis of samples from the Ae horizon lysimeter are reported in Tables 20 and 21. In samples collected from below the Ae horizon the concentration of polyphenols is lower and the volume of samples are smaller in the early portion of the growing season compared to concentrations in samples from the LFH lysimeter at the same time of year. This is a clear indication that polyphenols in solution are interacting with soil materials in the Ae horizon. In late fall the concentration of polyphenols returned to levels comparable to those of the LFH horizon samples. Seasonal means for polyphenol concentration in the Ae lysimeter samples are very similar to mean values for LFH lysimeter samples. Values of polyuronide and carbohydrate

Table 20. Mean monthly concentration (mg/l) of cations and pH of the lysimeter samples from the Ae horizon 1977.

	May	June	July	Aug	Sept	$\bar{x}$	s
K	11.5	40.0	12.3	24.2	-	22.2	13.3
Na	5.6	17.8	5.0	4.6	-	8.3	6.5
Ca	1.3	1.3	1.4	0.9	-	1.2	0.2
Mg	1.3	1.3	0.7	1.1	-	1.1	0.3
Fe	5.8	5.9	5.6	14.2	5.7	7.5	3.7
Al	10.7	10.7	12.9	25.2	9.8	13.9	6.4
Si	0.8	0.9	0.7	0.9	0.6	0.8	0.1
pH	7.0	6.6	7.2	7.4	7.2	-	-

Table 21. Mean monthly concentration (mg/l) of cations, organic constituents and pH of lysimeter samples from the Ae horizon 1978.

	April	May	June	July	Aug	Sept	Oct	Nov	$\bar{x}$	s
Polyphenols	-	2.4	1.0	-	-	4.3	1.3	5.0	2.8	1.8
Polyuronides	-	10.1	10.5	-	-	12.8	8.0	8.0	10.0	2.0
Carbohydrates	-	7.9	12.0	-	-	14.5	10.5	8.0	10.5	2.8
K	-	26.4	17.9	-	-	20.1	20.2	18.7	20.6	3.4
Na	-	3.1	1.7	-	-	5.0	2.5	1.6	2.8	1.4
Ca	-	10.9	6.8	-	-	6.7	6.2	6.5	7.4	2.0
Mg	-	2.5	1.5	-	-	1.9	1.5	1.6	1.8	0.4
Fe	-	0.4	0.7	-	-	2.3	3.0	1.6	1.6	1.1
Al	-	0.0	0.0	-	-	4.5	5.7	2.9	2.6	2.6
Si	-	0.2	0.5	-	-	0.9	0.9	0.8	0.7	0.3
pH	-	7.4	6.7	-	-	7.1	7.4	7.0	-	-

concentration remain at levels close to those of the LFH horizon samples throughout the year. However, since the volume of samples taken from the Ae lysimeter were significantly smaller than those from the LFH lysimeter (10 - 30 ml compared to 30 - 60 ml) it must be concluded that an interaction between the soil material of the Ae horizon and polyphenols, polyuronides, and carbohydrates in solution is occurring. The loss of organic constituents from solution may be attributed to polymerization, complexation with inorganic constituents, or microbial attack. The evidence suggests that polyphenols are removed from solution much more readily than polyuronides or carbohydrates, particularly in the early months of the growing season.

The presence of organic matter in the soil solution moving into the Bt horizon indicates that lessivage is accompanied by the movement of soluble organic constituents. Mel'Nikova and Kovenya (1974ab) note that the presence of mobile organic matter favours clay migration.

There have been reports in the literature (Duchaufour 1974; Mel'Nikova and Kovenya 1974ab) that iron and clay migrate into the B horizon simultaneously. Analysis of leachates from the Ae lysimeter (Tables 20 and 21) shows conclusively that lessivage involves the movement of Fe and Al into the Bt horizon. Concentrations of Fe and Al in solution are higher in 1977 than in 1978 in the samples from the Ae lysimeter. Differences in Fe and Al concentrations may be attributed to differences in the intensity and duration of precipitation and to interactions with soil materials. Heavy precipitation causes rapid movement of

water through the soil profile. This favours surface interactions but does not favour dissolution reactions. Slow percolation through the profile of solutions containing organic constituents favours the removal of Fe and Al from mineral structures. Since clay minerals present the greatest surface area to the leaching waters and the ratios of Fe to Al are close to those for clay minerals it can be concluded that the majority of Fe and Al found in solution result from weathering of clay minerals in the Ae horizon. The pH of the leaching solution should also influence concentrations of Fe and Al, higher concentrations would be expected under more acidic conditions. Values of pH of the leaching solution for both years are close to neutrality. The solubility of hydroxides of Al at these pH's is very low, yet concentrations as high as 25 mg/l were found. The conclusion that must be drawn is that Al in solution in the lysimeter leachates is complexed with organic constituents. This suggests that organic constituents in solution play a very important role in mineral weathering and in cation movement in Luvisolic soils.

Values of Si concentration show very little variability and tend to be slightly less than 1 mg/l. These values seem to be low considering that the most probable solubility of quartz has been reported to be 3 mg/l. However, the range of reported values is quite variable (0 - 14 mg/l, Wilding et al. 1977). Low Si concentrations in lysimeter leachates are attributed to nonequilibrium conditions. This suggests that while Al and Fe are being removed from the Ae horizon, Si is left behind as amorphous Si or in the remnants of clay mineral structures. This

finding may explain siliceous coatings and the ashy appearance of the Ae horizon.

The concentrations of major cations in samples from the Ae lysimeter in decreasing order are K, Ca, Na, Mg, as per the canopy drip samples and LFH horizon samples. The order of concentration is the same but there is some variability in actual concentrations. The ratios of K to Mg and K to Ca are wider in Ae leachates compared to LFH leachates.

There is some evidence to suggest that a portion of the K passing through the Ae horizon is retained on the exchange complex. Exchangeable K in the Ae horizon ranges from 4 - 8% of the total exchange capacity while in the Bt horizon K occupies less than 4% of exchange sites. Since the ratio's of K to Ca and K to Mg are wider for Ae samples, it is apparent that Ca and Mg are being removed from the soil solution as well.

The frequency of collection of samples and the volume of samples from the Ae lysimeter are lower than those from the LFH lysimeter. The volume of samples from the Ae lysimeter ranged from 10 - 30 ml whereas those from the LFH lysimeter ranged from 30 - 60 ml. The change in frequency and volume of samples may be attributed to a number of factors: the uptake of water by growing plants, evaporation and lateral flow of water.

Very few samples were obtained from the Bt horizon lysimeter and those obtained were quite small in volume (2 - 10 ml). The results of analysis of these samples are reported in Tables 22 and 23. The frequency and volume of Bt lysimeter samples suggests that the movement of free water

Table 22. Mean monthly concentration (mg/l) of cations and pH of the lysimeter samples from the Bt horizon 1977.

	May	June	July	Aug	Sept	$\bar{x}$	s
K	4.5	2.5	3.0	-	-	3.3	1.0
Na	6.9	3.2	4.0	-	-	4.7	1.9
Ca	4.2	3.4	5.5	-	-	4.4	1.1
Mg	1.4	1.5	1.5	-	-	1.5	0.1
Fe	0.6	0.8	-	-	-	0.7	0.1
Al	0.0	0.0	-	-	-	-	-
Si	0.6	0.7	0.7	-	-	0.6	0.1
pH	6.4	-	-	-	-	-	-

Table 23. Mean monthly concentration (mg/l) of cations, organic constituents and pH of lysimeter samples from the Bt horizon 1978.

	May	June	July	Aug	Sept	Oct	Nov	$\bar{x}$	s
Polyphenols	–	–	18.0	–	23.5	–	–	20.3	4.2
Polyuronides	–	–	5.0	–	8.0	–	–	6.5	2.1
Carbohydrates	–	–	0.0	–	0.0	–	–	–	–
K	–	–	2.4	–	3.2	–	–	2.8	0.6
Na	–	–	9.3	–	3.5	–	–	6.4	4.1
Ca	–	–	2.4	–	8.2	–	–	5.3	4.1
Mg	–	–	7.0	–	2.1	–	–	4.6	3.5
Fe	–	–	0.7	–	0.3	–	–	0.5	0.3
Al	–	–	0.0	–	0.0	–	–	–	–
Si	–	–	0.6	–	0.7	–	–	0.7	0.1
pH	–	–	–	–	–	–	–	–	–

through the Bt horizon is not a frequent occurrence. This indicates that illuviation occurs in the upper Bt horizon more frequently than in the lower Bt. Movement of free water into the middle Bt horizon occurs only after significant additions of water to the solum from heavy rainfall or snowmelt. This is supported qualitatively by Figures 9 and 10 which show collection dates, precipitation, and soil moisture status.

Analysis of samples from the Bt lysimeter indicates the presence of organic constituents. Polyphenols were detected in concentrations substantially greater than those in solutions leaching through the Ae horizon. Increased concentrations of polyphenols in Bt leachates may be a result of the reduction in sample volume and the lack of interactions between these constituents and soil materials in the Bt horizon. A 50% drop in polyuronide concentration occurred between the Ae and the middle of the Bt and carbohydrates were not detected in the Bt leachates.

The presence of organic constituents in solution may explain the slight bulge of organic C in the Bt horizon. Since these solutions were clear and contained no colloidal material it can be concluded that organic matter is moving into the Bt horizon independently of clay migration. The illuviation of soluble organic constituents explains, at least partially, the greater quantities of C and N on ped exteriors as reported by Heil and Buntley (1965); and Boule and Hole (1959). This does not preclude the possibility that illuviation of clay-organic complexes on ped exteriors is responsible for elevated C and N

values.

The results also indicate that Fe is moving through the Bt horizon. It is probable that Al is being illuviated on ped exteriors or argillans in the upper Bt horizon since Al was not detected in the Bt lysimeter. This is supported by the marked bulge in dithionite-citrate-bicarbonate extractable and pyrophosphate extractable Al in the Bt1 horizon. Fe concentration dropped significantly from the levels detected in the Ae lysimeter. This suggests that much of the Fe was removed from solution before reaching the collection device in the Bt horizon. These results confirm the proposal of Duchaufour (1971) that iron moves into the B horizon during lessivage. Aluminum was not detectable in Bt lysimeter samples in 1977 or 1978, however samples from the Ae lysimeter indicate that Al did migrate into the Bt horizon. One must conclude that Al is removed from solution in the upper B horizon either through interaction with suspended colloidal material or by interaction with soil material along cracks and pores through which water is passing.

Detectable quantities of all major cations, except Al, are present in lysimeter samples from the Bt horizon. The order of concentration is changed significantly from samples collected from the LFH and Ae horizons. In decreasing order, the concentration in the Bt samples is Na, Ca, K, Mg. Clearly Na is passing through the upper portion of the profile uninterrupted. On the other hand, K concentration drops substantially in samples from the Bt horizon compared to samples from the LFH and Ae lysimeters. The ratio of K to Mg and K to Ca are very narrow in

samples from the Bt horizon. Most probably some K is being retained on the exchange complex of the soil and some is being removed by plants. It was noted in the discussion of micromorphology that argillans in the upper Bt horizon contained significantly more K than those deeper in the profile. This was attributed to a greater content of mica in the argillans of the upper Bt horizon. Exchangeable K in the upper Bt horizon is only 1 - 2% greater than that in lower horizons. Since we know from this leachate analysis that K is being retained in the upper Bt, it can be concluded that some of the K is entering the interlayer positions of hydrous micas and possibly smectite in argillans, along pores and in vughs in the upper Bt horizon. This interaction would alter the manner in which the argillans refract polarized light creating a highly micaceous appearance.

As discussed earlier in this section quantities of Fe, Si, and Al were detectable in the leachates from the Ae horizon and Fe and Si were present in Bt leachates. These elements were not detectable in samples of canopy drip or LFH leachate. Ugolini et al. (1977) report the presence of variable quantities of these elements in the soil solution of a Podzolic soil (Cryandept). In particular they report Si values in the range of 3 - 5 mg/l. In this study it was found that Si values were in the range 0.6 - 0.9 mg/l. Values of Al concentration reported by Ugolini et al. were in the range 0.3 - 0.9 mg/l while Fe concentrations reported were lower (0.05 - 0.1 mg/l). Values of Al and Fe concentration found in this study (Tables 22 and 23) tend to be higher than those reported by Ugolini et al. In 1978 Fe ranged

from 0.4 - 3.0 mg/l and Al concentration fell between 0.0 - 5.7 mg/l. In 1977 values for Fe and Al in soil solution were very high, particularly in Ae lysimeter samples where Fe ranged from 5.6 - 14.2 mg/l and Al ranged from 9.8 - 25.2 mg/l. The higher concentrations of Fe and Al in solution in a Luvisolic soil compared to a Podzolic soil presents an interesting anomaly. Examination of the Podzolic pedon description at Findley Lake indicates that the A2 (Ae) horizon is developed in volcanic ash. This makes comparisons between these cases very difficult.

While lessivage has been shown to be the predominant soil forming process in the genesis of the Breton soil, the presence of Si, Fe, and Al in soil solution indicates that some dissolution of minerals and translocation of the weathering products is occurring. Organic matter is mobile in the profile and there is a very slight accumulation of organic C in the Bt horizons. This shows that, as well as lessivage, a type of podzolization is also operative in the genesis of this Luvisolic soil. Russian authors have often alluded to the process of pseudo-podzolization; this study may have provided in situ evidence of this process.

The mineralogy of the profile clearly indicates a single suite of clay minerals. This has been used to prove that in fact lessivage is the dominant soil forming process. There is no evidence that the weathering products that have migrated to the Bt horizon are reforming to produce new minerals. Consideration of the free energy of formation of smectite and mica makes it doubtful that clay minerals are being formed from amorphous oxides and hydroxides of Si, Al, and Fe. It is suggested that at

least some of the Si, Al, and Fe remain in the solum as amorphous compounds and the remainder removed to the groundwater.

Colloidal Leachate Analysis

Chemical Analysis

Some of the samples collected from the Ae lysimeter contained colloidal material in suspension. This material was separated from the liquid sample by centrifugation. The liquid samples were analyzed as described earlier while colloidal samples were analyzed as outlined in Figure 13. The 1977 sample was extracted with sodium citrate and ammonium oxalate, however the results of analysis indicated that these treatments were unnecessary. The results of the analysis of liquid samples from which colloidal material was separated are found in Table 24.

The liquid samples from which colloidal material was separated had concentrations of polyphenol much lower than the mean monthly values for all samples. Concentrations of polyuronides and carbohydrates are comparable to mean monthly averages. The observed decrease in polyphenol concentration in lysimeter samples containing colloidal material suggests that migration of clay from the Ae horizon may be related to a removal of polyphenols from solution. This suggestion is based on the analysis for polyphenol content in the two 1978 samples from the Ae horizon. Therefore the results are not conclusive.

The concentrations in solution of K and Na are quite

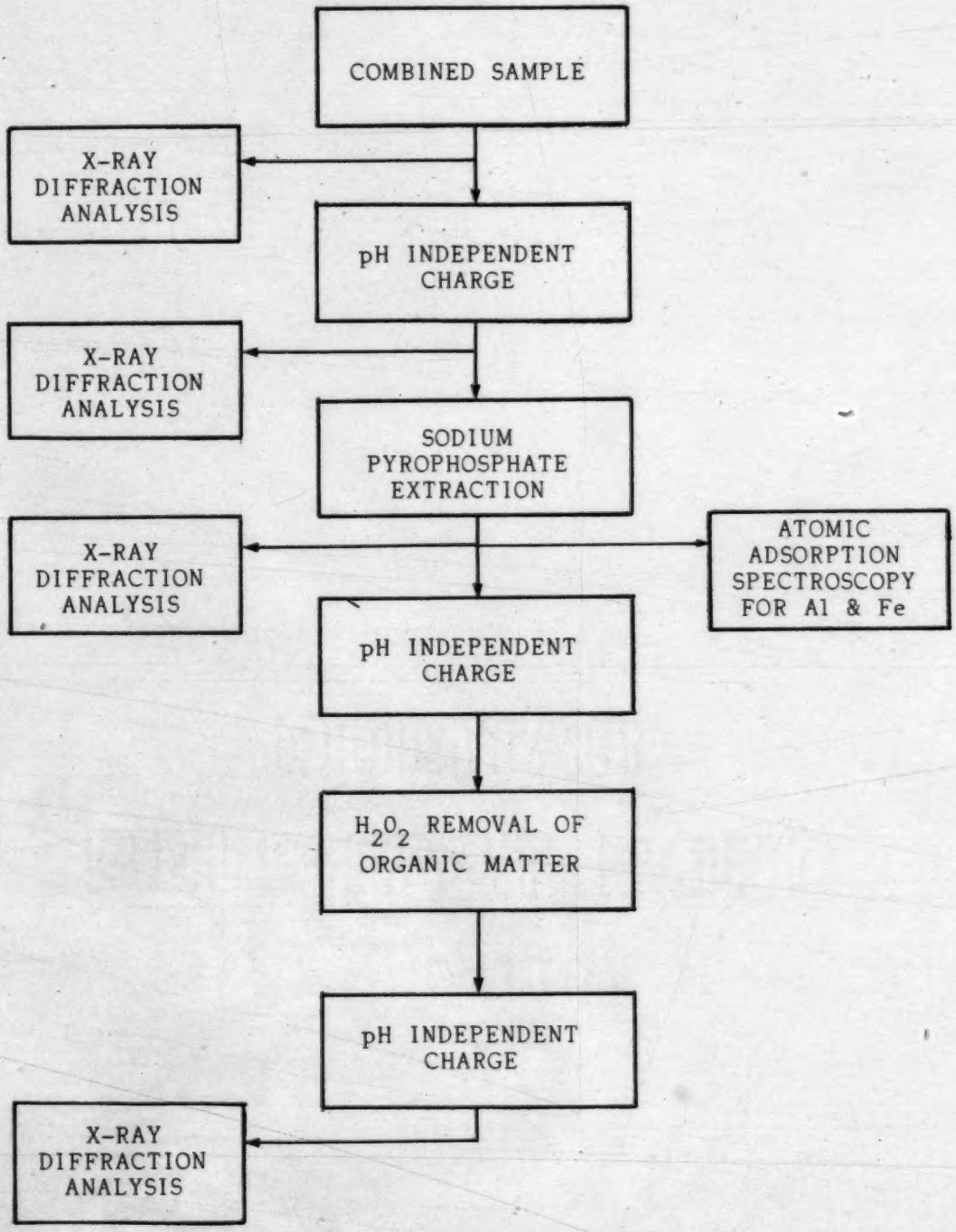


Figure 13. Flowchart of colloidal material analysis.

Table 24. Concentration (mg/l) of cations, organic constituents and pH on dates when colloidal material was collected from Ae lysimeter samples.

Date	20 May 1977	8 July 1977	5 Aug 1977	12 Aug 1977	26 Aug 1977	30 Aug 1977	25 Oct 1978	8 Nov 1978
Polyphenol	-	-	-	-	-	-	1.3	5.0
Polyuronide	-	-	-	-	-	-	8.0	8.0
Carbohydrate	-	-	-	-	-	-	10.5	8.0
K	11.5	13.2	22.7	35.0	15.0	-	20.2	18.7
Ca	1.3	2.0	0.7	1.2	1.1	-	6.2	6.5
Na	5.6	7.6	2.4	10.0	1.5	-	2.5	1.6
Mg	1.3	1.0	0.5	1.5	1.0	-	1.5	1.7
Si	0.8	0.7	-	1.0	0.9	0.6	0.9	0.8
Al	10.7	2.7	23.1	13.4	10.7	9.8	5.7	2.9
Fe	5.8	1.7	2.5	7.0	5.5	5.7	3.0	1.6
pH	7.0	7.2	-	7.1	6.9	7.2	7.4	7.0

variable in samples containing colloidal material. Concentrations of Ca and Mg are low and quite constant. Mean concentrations of Ca computed for all samples taken in any month are generally higher than the values obtained for samples containing colloidal material. This suggests that Ca is tied up during clay migration. There are no significant differences between K concentrations during the year and concentrations in samples containing colloidal material.

Depressed values of polyphenol and Ca concentrations suggests that both are interacting with moving clays. One theory to explain the conjunction of clays and organic matter is the cation bridge hypothesis. A positively charged cation is thought to be attracted to the clay surface while the negatively charged organic molecule is attracted to the cation. The cation forms a bridge between the clay and the organic molecule (Greenland 1971).

In an attempt to ascertain whether clay-organic bonding is occurring during clay migration use was made of the pH independent charge determination. The charge on organic molecules is largely a result of ionization of hydrogen from carboxyl groups at the surface of the particles (Bear 1955). A decrease of pH causes a decrease in the ionization of the carboxyl group. Charge sites on clay minerals resulting from isomorphous substitution are unaffected by pH, consequently an increase of pH independent charge following organic matter removal would indicate that charge sites on the clay mineral were blocked through bonding with the organic constituents.

If organic molecules are blocking charge sites on clay mineral surfaces then a positive change in pH independent charge should occur following the removal of organic matter. Consequently during analysis of the colloidal leachate the first step was to determine the pH independent charge of the leachates before and after pyrophosphate extraction. Pyrophosphate is known to remove only the more readily soluble organic compounds; therefore a final treatment with hydrogen peroxide (H_2O_2) was used to completely destroy all organic matter. Extraction with acid ammonium oxalate and sodium citrate were also included in the procedure to determine if amorphous Fe and Al compounds or interlayer Al-hydroxy groups were present in the colloidal leachates.

X-ray diffraction was used as a qualitative measure of the effect of each treatment on the colloidal leachates. Preliminary X-ray diffraction analysis of the raw or untreated colloidal material showed elevated background in the 14 - 16 Å peak range with a more or less distinct peak at 10 Å. The patterns tended to sharpen on heating to 550°C. The resolution of the elevated background was considered to be a very important part of the analysis.

The composite sample of colloidal material for 1978 was divided into two fractions (A and B) on the basis of its appearance following separation of the material from liquid sample. The A fraction remained in suspension in distilled water whereas the B fraction was flocculated on the bottom of the test tube. The two fractions differed in optical properties; the A

fraction being lighter in colour than the B fraction. The B fraction exhibited the optical properties of biotite under the petrographic microscope. Preliminary X-ray diffraction analysis indicated that the A fraction was amorphous to X-rays whereas the B fraction exhibited a 10 Å peak and an elevated background between 14 and 17 Å. The two fractions were analyzed separately.

The results of pH independent charge determination of the 1977 colloidal sample are reported in Table 25. The analysis was duplicated two consecutive times on the same sample and the results show a net increase of charge following pyrophosphate extraction. There is, however, considerable variability between the first and second duplicate.

Table 25. pH independent charge before and after $Na_4P_2O_7$ treatment 1977 (meq/100g).

	Charge	$\bar{x}$
Before $Na_4P_2O_7$	67.9 23.5	55.7
After $Na_4P_2O_7$	155.4 81.6	118.5

The variability was found to result from the nature of the determination. In an attempt to obtain a consistent result for pH independent charge for the 1978 samples of colloidal material the procedure was repeated 9 times.

Figures 14 and 15 are a graphical representation of the change in pH independent charge over the 9 determinations as well as the changes following $Na_4P_2O_7$ treatment and H_2O_2

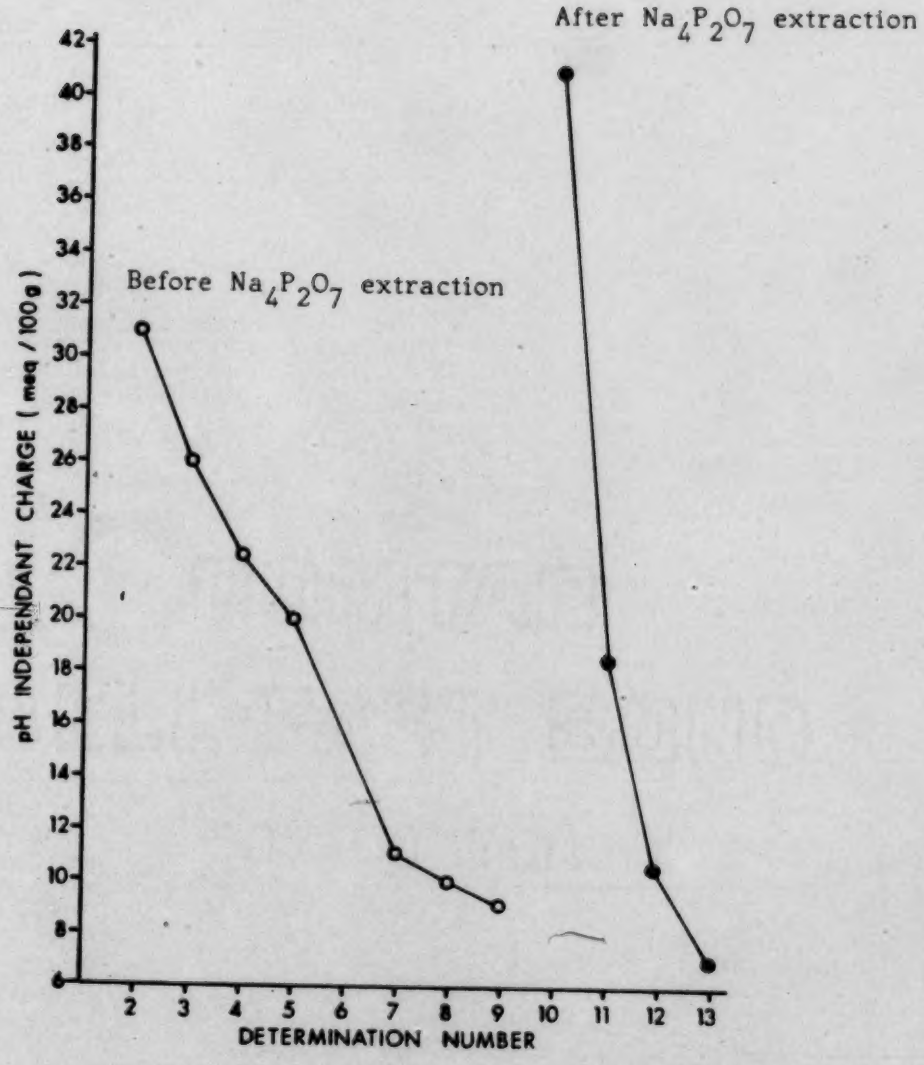


Figure 14. Graphical representation of the change in pH independent charge before and after $Na_4P_2O_7$ treatment for the A fraction of the 1978 colloidal material.

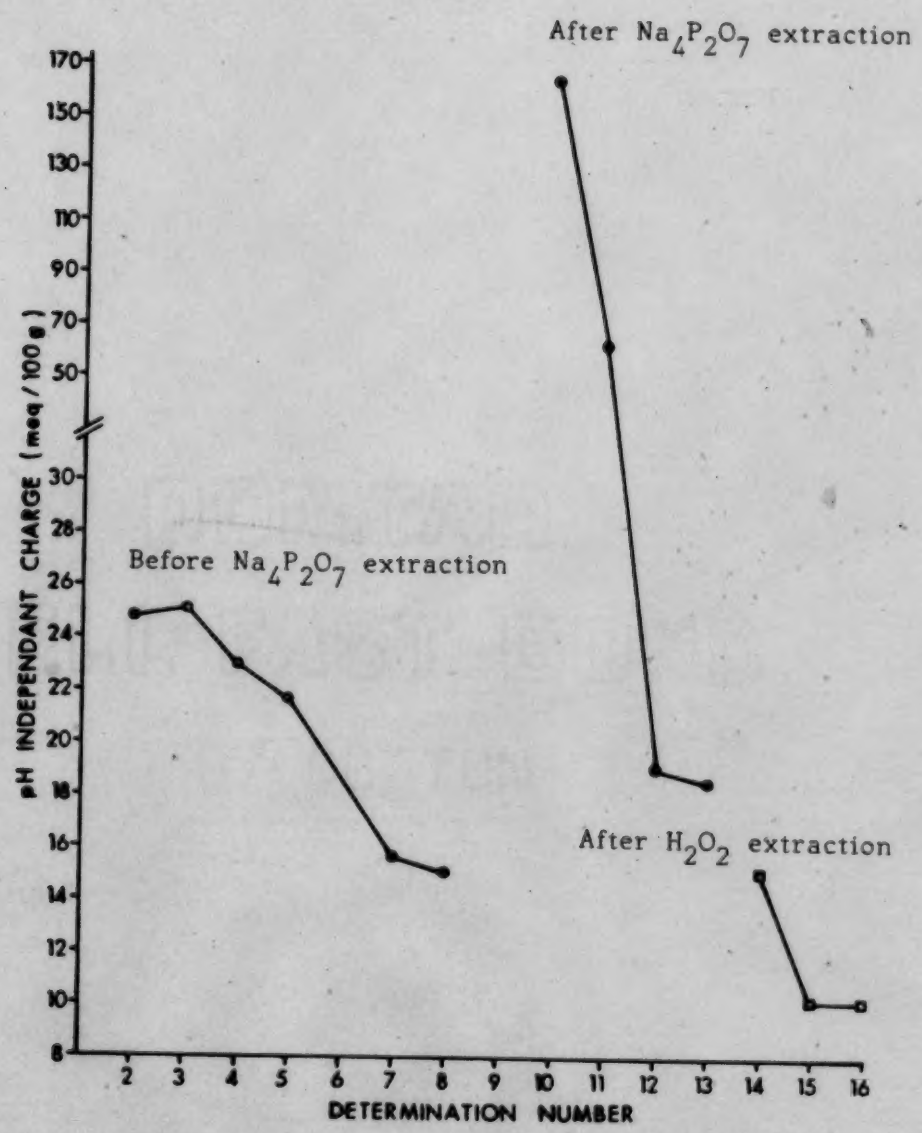


Figure 15. Graphical representation of the change in pH independent charge following $Na_4P_2O_7$ treatment and H_2O_2 treatment for the B fraction of the 1978 colloidal material.

treatment for the A and B fractions. It is clear that a continuous decline of charge occurred over the 9 determinations. This explains the decrease of pH independent charge between the first and second determinations on the 1977 sample. The continuous decline in charge with repeated determinations was not expected as it was assumed that the procedure was non destructive. The results indicate that a loss of permanent charge sites occurred during treatment. Either charge sites are blocked or they are removed from the exchange complex. The most logical answer would be the loss of exchange sites via a weathering reaction resulting from the use of KCl at a pH = 3. Protonation of bonds on the clay mineral will result in the liberation of Al, Si, and Fe into solution. Loss of these cations from the mineral would cause a decrease in charge. The hydroxides of Al could block exchange sites, particularly in the interlayer position. This hypothesis is supported by the presence of Al and Fe in supernatant solutions of KCl extractions.

Following extraction of 1978 colloidal material with $Na_4P_2O_7$ an increase in pH independent charge occurred for both the colloidal fractions. It is assumed that the increase in charge following pyrophosphate extraction indicates that pyrophosphate extractable (organic) compounds are blocking exchange sites on clay mineral surfaces. The blocking effect of these compounds is greater in the lighter coloured, more highly dispersed A fraction than in the B fraction.

Following complete removal of organic compounds using H_2O_2 the pH independent charge of the B fraction remained unchanged

from previous determinations. Results of pH independent charge following H_2O_2 treatment of the 1977 sample and the A fraction are not reported as both samples were quite small at this stage of analysis.

Results of analysis of $Na_4P_2O_7$ extracts are reported in Table 26. Significant differences exist in the amounts of each element. In both 1977 and 1978 the amount of pyrophosphate extractable Fe in the colloidal samples is greater than the amount of pyrophosphate Al. This is in accordance with the theory of lessivage that Fe migrates concurrently with clay. The results indicate that Al is also mobile in the solum during lessivage. Analysis of liquid samples indicated that Fe was moving in solution; pyrophosphate extraction has indicated that Fe is also moving in association with organic matter which may be complexed with clay.

The amount of pyrophosphate extractable Fe and Al was lower by one hundred times in 1978 compared to 1977 whereas there was significantly more pyrophosphate extractable C in the 1978 sample compared to the 1977 sample. These differences are undoubtedly a function of the rate of movement of leaching solutions through the soil. The 1977 sample of colloidal material was an accumulation of a number of samples collected over the whole season whereas the 1978 sample was the result of one period of heavy precipitation.

The increase in pH independent charge following pyrophosphate extraction was greater for the 1977 sample than for the 1978 sample. This indicates that a greater degree of

bonding between clays and organic constituents is occurring in the 1977 sample. However, there is significantly more C in the 1978 sample which suggests that during lessivage organic matter moves in suspension independently of clay.

Table 26. Pyrophosphate extractable Al, Fe and C of colloidal material expressed as percentages of sample dry weight.

	% Al	% Fe	% C
1977	0.22	0.72	0.94
1978 A	0.01	0.04	3.02
1978 B	0.01	0.04	1.43

Results for oxalate and citrate extractable Fe and Al for the 1977 sample are reported in Table 27. The oxalate extraction is thought to remove amorphous (to X-rays) Fe and Al compounds. The results indicate there is nearly twice as much oxalate extractable Fe as Al. This provides further evidence that the process of lessivage involves the movement of Fe, Al, and clay. It is not clear if this "amorphous" Fe and Al is moving independently of clay or if the two are complexed during the process. Some of this Fe and Al may be present as a result of the pH independent charge determinations which is thought to remove cations from the clay mineral structures. These hydrated cations remain in the sample as amorphous compounds probably in conjunction with clay minerals.

Table 27. Oxalate and citrate extractable Fe and Al for the 1977 colloidal sample.

Oxalate extractable Fe	0.63%
Oxalate extractable Al	0.35%
Citrate extractable Fe	0.66%
Citrate extractable Al	0.42%

The Na citrate extraction is designed to remove interlayer Al - hydroxy compounds from clay minerals. Although the citrate extraction did remove some Fe and Al from the sample X-ray diffraction analysis indicated that interlayer Al - hydroxy groups were not present in the sample. It must also be remembered that the two determinations (oxalate and citrate extraction) may be responsible for removing Al and Fe from clay mineral structures and for destroying amorphous Fe and Al. For these reasons it was decided to eliminate oxalate and citrate extractions from the analysis of the 1978 sample of colloidal leachate.

X-ray Diffraction Analysis

X-ray diffraction patterns of the colloidal leachates are presented in Figures 16 - 18 and in Appendix C. X-ray diffraction patterns of the untreated 1977 colloidal sample revealed a peak at 10 Å and an elevated background between 10 and 16 Å. The elevated background persisted through treating to 300°C, however it disappeared on heating to 550°C (Figure 16). These results prompted the investigation as outlined earlier since the observed X-ray diffraction patterns suggested the presence of

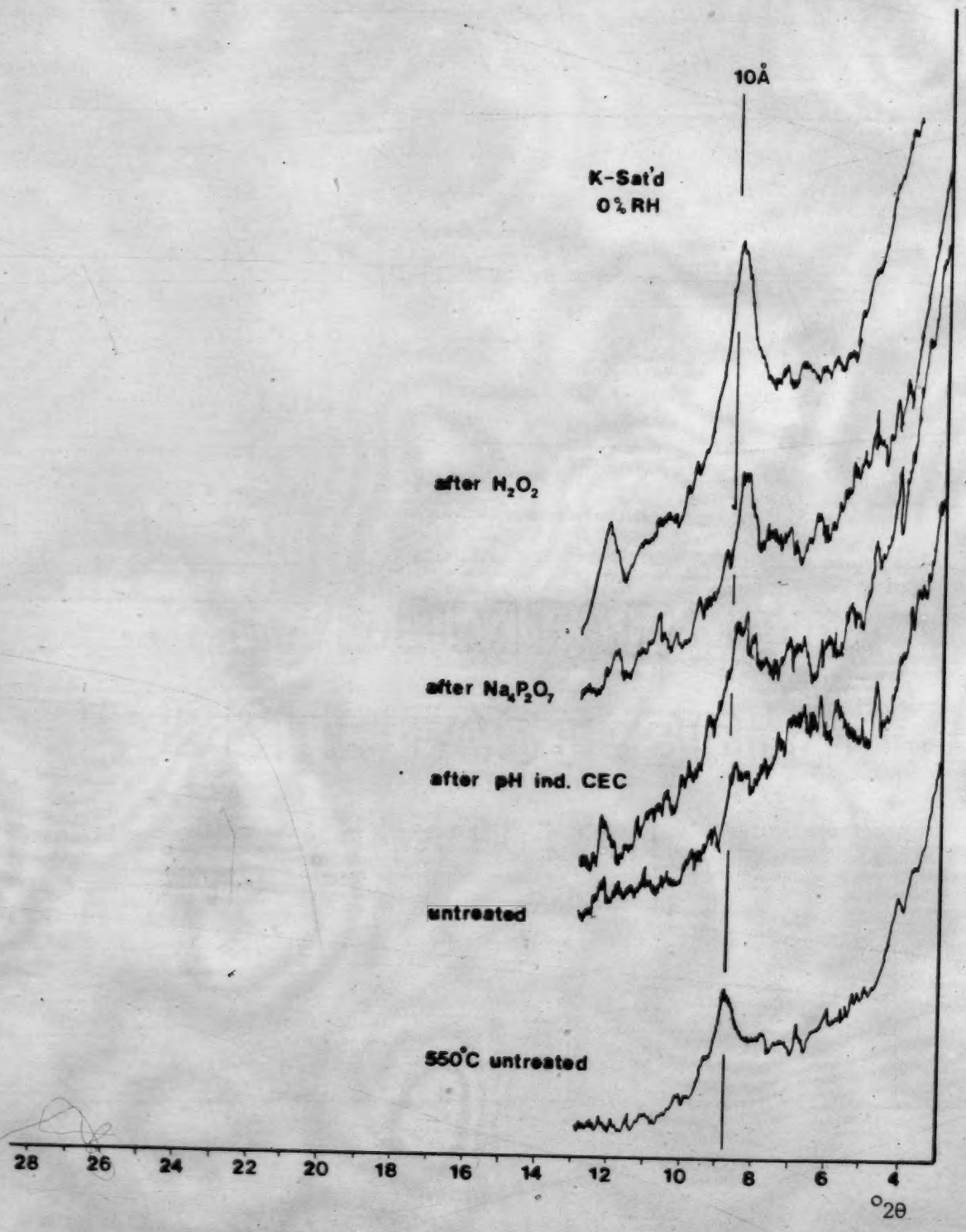


Figure 16. Composite X-ray diffractogram of the 1977 colloidal material.

organic material in the colloidal leachates. The elevated background was thought to be a result of organic matter interfering with the uniform diffraction of X-rays from clay mineral structures by reducing the degree of orientation of the minerals on the glass slide and by interfering with the interlayer position of expandible minerals. The interference may result from clay-organic bonding or a non-bonding physical interference. Heating to 550°C causes oxidation of the organic matter resulting in resolution of the elevated background.

The interaction of clays and organic matter has been reported in the literature by Schnitzer and Kodama (1977). It is apparent from their studies, that on heating, organic compounds can be protected from oxidation by the presence of clays. These authors report specific and measurable changes of d-spacing of montmorillonite resulting from interlayer adsorption of fulvic acid at varying pH values. This is very difficult to conceptualize given the molecular weight and size of fulvic acid.

Natural clay-organic complexes found in soil are discussed by Moum et al. (1973); Perez Rodriquez et al. (1976); and Turchenek and Oades (1976). Perez Rodrequez et al. (1976) discuss the mechanics of montmorillonite - protein interactions. Their work indicates that a number of mechanisms are possible and that interaction between clay and organic molecules does not necessarily produce ordered systems. Partial entry of organic matter, bonded to the clay mineral surface, into the interlayer position would best explain the expansion of d-spacing by organic compounds. The presence of organic constituents in the

interlayer position or on the exterior surfaces of clay minerals results in the unresolved X-ray diffraction peaks.

Determination of pH independent charge involved saturation of the colloidal sample with K and sonification. Following these treatments the 10 Å peak persisted and although the elevated background between 10 - 16 Å is present it is less pronounced than in the untreated sample. This may be a result of uniform cation saturation or of sonification causing dispersion of clays and organic matter. The elevated background is noted to have disappeared on heating to 550°C.

Treatment of the 1977 sample with pyrophosphate caused a distinct sharpening of the 10 Å peak at 0% R.H. and the loss of the elevated background which had persisted through pH independent charge determinations. It is not clear whether the organic constituents were actually bonded to the clay minerals or whether their physical presence was causing the disruption of X-ray diffraction. The increase in pH independent charge following pyrophosphate extraction would suggest that bonding was occurring.

Removal of amorphous Al and Fe and of interlayer Al by extraction with acid ammonium oxalate and sodium citrate resulted in some peak sharpening and the resolution of a peak in the 12 Å region. A reappearance of the elevated background occurred following oxalate treatment; it disappeared on heating and can be attributed to retention of amorphous compounds in the sample.

Complete removal of organic matter using H_2O_2 produced

significant peak sharpening of the X-ray diffraction pattern. In particular peaks at 7 and 5 Å which had been weak or absent were accentuated following extraction with H_2O_2. Clearly the remaining organic components were responsible for disrupting diffraction of incoming X-rays from the clay mineral structures. It is probable that this results from a physical disruption of clay orientation on the glass slide. Pyrophosphate extraction is responsible for removal of relatively soluble humified organic compounds thus any remaining organics would be removed by H_2O_2.

X-ray diffraction analysis of the A and B fractions of the 1978 sample yielded results somewhat different to those of the 1977 sample (Figures 17 and 18). Extraction with pyrophosphate tended to clean up the patterns, in particular the 10 Å peak is more pronounced. The elevated background remained following pyrophosphate extraction and did not disappear following heating to 550°C.

Complete removal of organic matter from the A and B fractions caused very distinct sharpening of the 10 Å peak, however unresolved peaks remained in the 12 - 14 Å range. These peaks are thought to be due to the presence, in small quantities, of certain mineral species and to amorphous inorganic compounds remaining in the sample following repeated pH independent charge determination. It is also noted that quartz peaks are present on the pattern after H_2O_2 treatment.

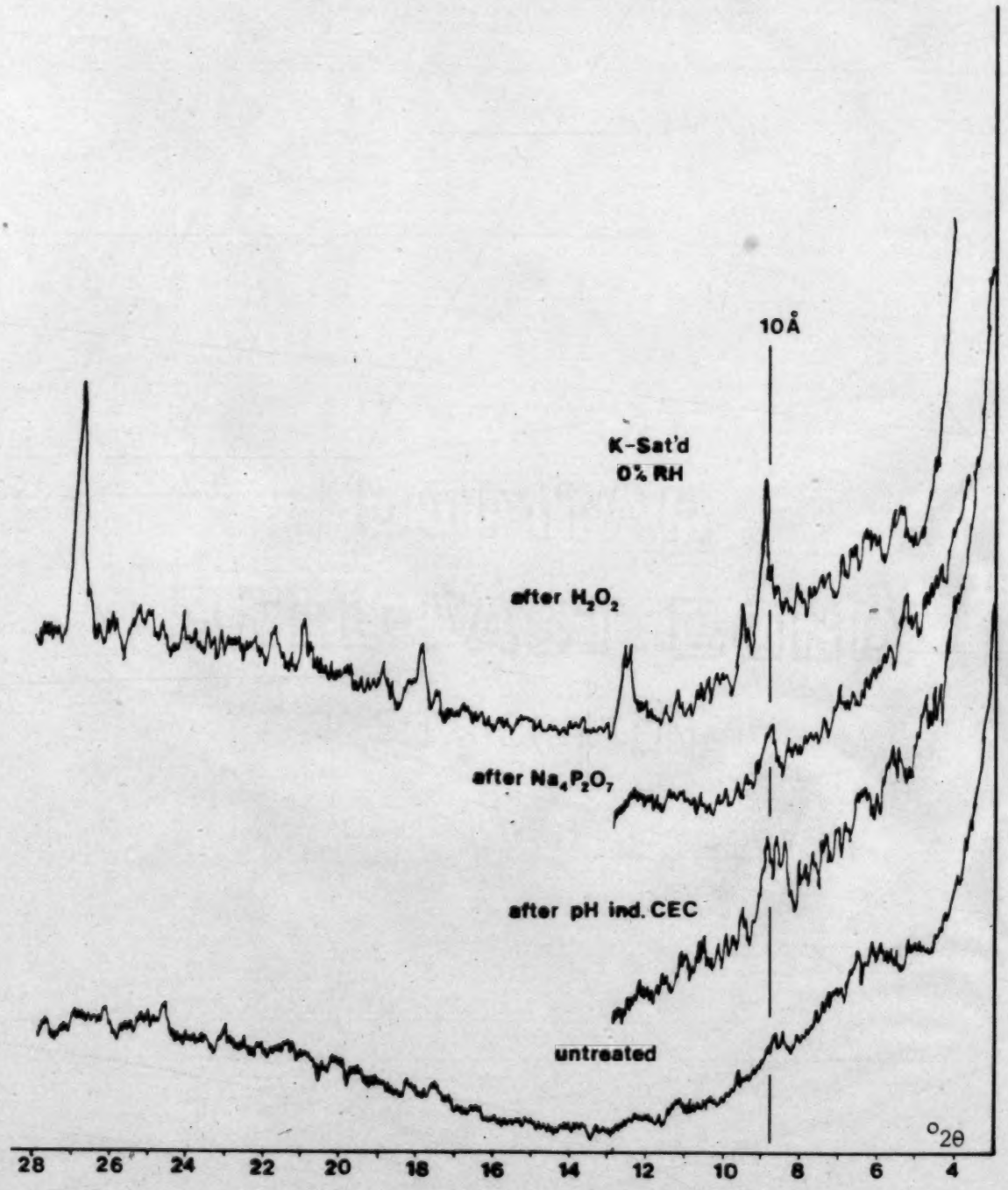


Figure 17. Composite X-ray diffractogram of the A fraction of the 1978 colloidal material.

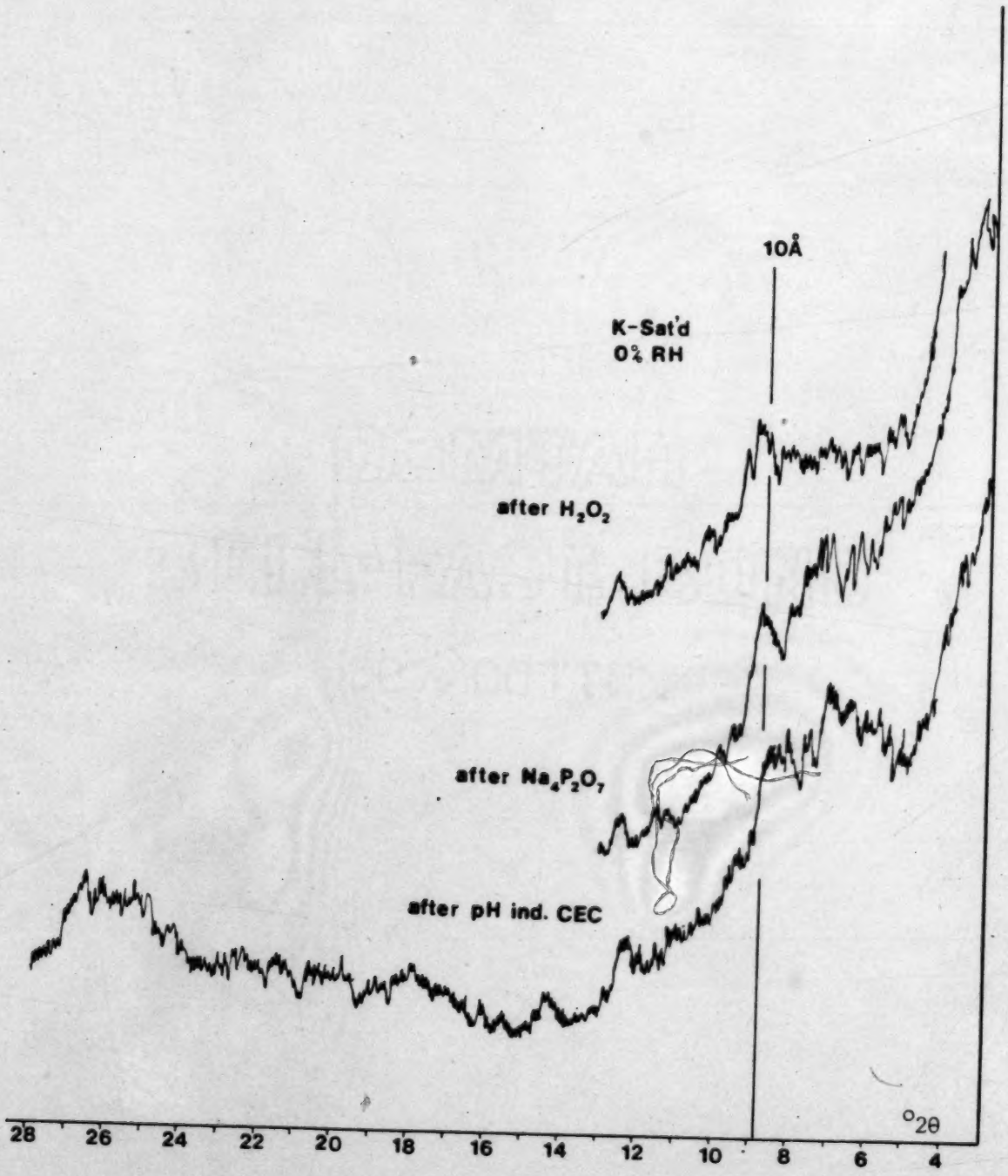


Figure 18. Composite X-ray diffractogram of the B fraction of the 1978 colloidal material.

Scanning Electron Microscopy of Colloidal Material

Scanning electron microscopy is useful in studying the surface topography of very small particles. It was extremely difficult to isolate individual clay particles for study, consequently the surface and edges of a thick layer of clay particles were studied. Edges of individual clay minerals could be found and studied along the surface and edges of the layer of clay. Using a Kevex energy dispersive system it was possible to obtain the relative elemental composition of particles under study.

Of particular interest was the presence of silt sized quartz grains in these samples (both years). The first reaction to this finding was concern about the possibility of sloughing particles into the lysimeter collectors from the soil column. Silt sized quartz grains have been noted in argillan matricies; therefore it is logical to assume that those quartz grains found in lysimeter samples were moving simultaneously with clay during lessivage. It is easy to conceptualize the movement of quartz through the profile during periods of rapid water movement as occurred in the fall of 1978 when the colloidal samples for the year were collected in one sampling. Previously it was thought that silt sized grains that were present in argillans were derived from the soil matrix as a result of physical stress (shrink-swell and freeze-thaw cycles).

Clays appeared fuzzy under the scanning electron microscope (Figure 19a). It was not possible to resolve the edges of individual particles. Elemental analysis of the clays revealed

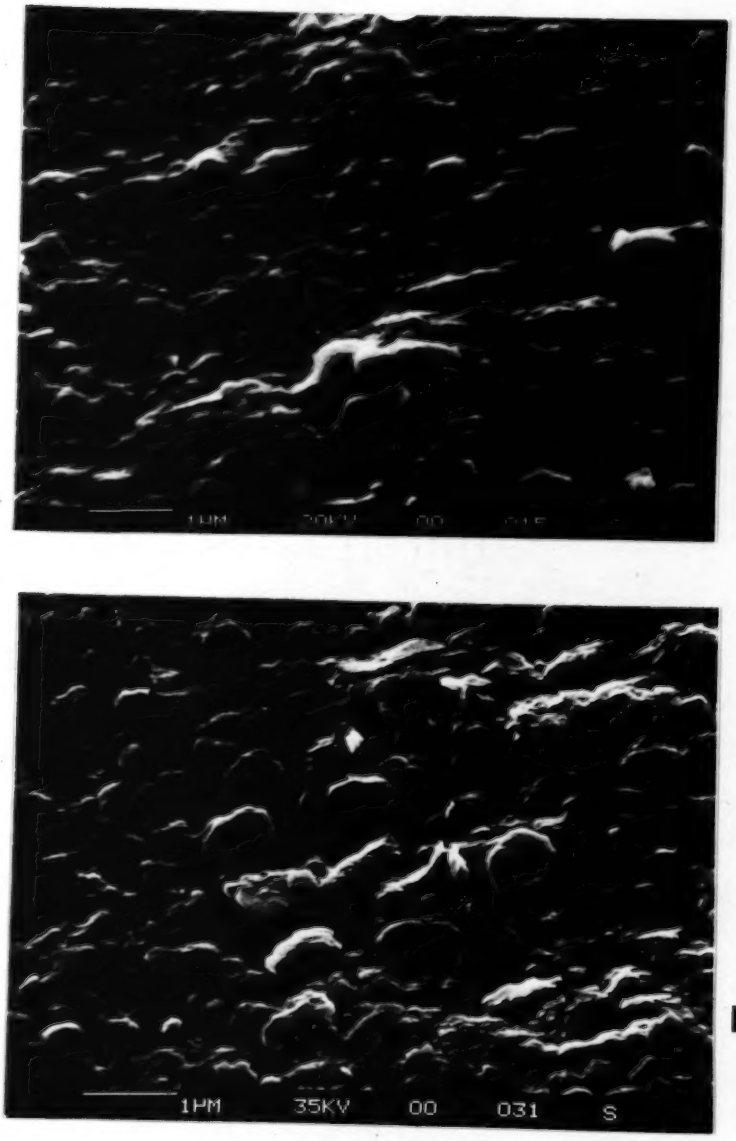


Figure 19. Scanning electron microgram of the B fraction of the 1978 colloidal material a) before H_2O_2 treatment, and b) after H_2O_2 treatment.

concentrations of Al, Si, K, and Fe. Some variability in the height of the Fe peak was noted; however, the peak heights of the other elements remained very constant. Morphology and surface texture of the clays did not change in response to pyrophosphate treatment. However, following H_2O_2 removal of organic matter a significant change in the surface characteristics of the clay is seen (Figure 19b). It is noted that the edges of surfaces of the clays are much sharper and lack the "fuzzy" appearance noted earlier. This suggests that the presence of organic matter is causing the fuzzy appearance of clay surfaces by adhesion to those surfaces. This is not born out by the change in pH independent charge following organic matter removal with peroxide. Thus if bonding between organics and clay is occurring in these pyrophosphate treated samples negative charge sites on the clays are not being blocked by the organic matter.

Mineralogy of Colloidal Material

It is apparent from X-ray diffraction analysis that mica is the most abundant clay mineral in these samples. This is supported by the pH independent charge of the sample which is far too low for smectites and in the range of mica and hydrous mica. It is clear from the X-ray patterns that a small quantity of an expandible mineral is present. Rehydration of oven-dried slides produced peaks in the 12 - 14 Å range and saturation with ethylene glycol produced a "smear" between 17 and 16 Å. It is thought that this smear is representative of smectite

expansion; resolution of the peak did not occur as the sample contains amorphous Al-hydroxides from the pH independent charge determinations. Miscellaneous peaks in the 12 - 14 Å range are present during analysis and are attributed to traces of "chloritized" minerals.

The significance of the mineralogy lies in the fact that mica is the mobile constituent in the soil profile. It is apparent from analysis of the pedon that it is the fine smectites which have accumulated in the Bt horizon as indicated by clay mineralogy of particle size distribution. However, colloidal leachate analysis indicates that mica is the mineral species moving in today's environment.

In the discussion of micromorphology it was noted that argillans in the upper horizons contained greater quantities of K than those lower in the profile and that they exhibited the optical properties of mica. It was postulated that argillans in the upper Bt horizons contained more mica than those in the lower solum. The mineralogy of the colloidal leachates further confirms this idea and suggests that illuviation is occurring in the upper B horizon at this stage of pedogenesis.

These findings shed light on the overall genesis of Luvisolic soils. Smectite which has become concentrated in the Bt and BC horizons of this soil must have migrated during an earlier stage of pedogenesis. It has moved furthest into profile with argillans being found at depths of 2.5 m. At the present stage of genesis it is the mica fraction of the clay mineral suite which is moving downwards into the B horizon. The results

suggest that mica is being illuviated into the upper Bt horizons whereas smectite has been carried into the lowest portion of the solum. It is clear that lessivage is a dynamic ongoing process which involves the movement of different species of clay (smectite and micas), iron, organic matter, and silt sized quartz grains.

CHAPTER V

SUMMARY OF DISCUSSION AND CONCLUSIONS

Analysis of canopy drip samples revealed that the order of cation concentration is K, Ca, Na, Mg. Very little difference exists between the cation concentrations for the aspen and white spruce canopy drip samples. Values of pH were close to neutrality for both species. These pH values are thought to result from high concentrations of K and the presence of bicarbonate in solution. It has been generally accepted that Luvisolic soils develop under moderately acidic conditions. The results of this study, however, indicated that this is not the case.

The order of cation concentration in lysimeter leachates from the LFH and Ae lysimeters was the same as that for canopy drip samples. The ratios of the cations to one another, however, are somewhat different. It is thought that K is being depleted from the leaching solution by plant uptake or through retention on the exchange complex. In samples from the Bt horizon lysimeter the order of cation concentration was Na, Ca, K, Mg. This change was attributed to the removal of cations from solution, particularly K.

The LFH horizon contains more water throughout the year than the mineral horizons, and fluctuations in moisture content are greater in the LFH horizon than in mineral horizons. Due to its high moisture holding capacity, the LFH tends to inhibit

water movement into the Ae horizon. A significant rainfall event is required to push water through the LFH into the Ae horizon.

The moisture content of the Ae horizon is the lowest of the mineral horizons. It fluctuates just above and below reported 1/3 bar moisture contents. This suggests that temporary water logging may occur which may result in Fe reduction and mobilization. The results indicate that the Ae horizon is very efficient at passing water vertically or laterally. This is thought to be a result of the texture and structure of the Ae horizon. The lateral flow of water may also influence the structure of the Ae horizon and may have played a role in the development of soil structure.

The moisture content of the Bt horizon is greater than that of the Ae horizon. Substantially more fluctuation in moisture content occurs in the Bt horizon than in the Ae horizon or at depth. Moisture contents at 90 cm and 225 cm are very constant throughout the year and are close to reported 1/3 bar moisture contents.

Examination of the Ae horizon in winter showed lenses of ice. These lenses accentuated the platy structure of the Ae horizon. There is no evidence, however, to suggest that this phenomenon is related to clay mobilization.

Soil temperature measurements indicated that during the months of May to August the soil solum is warming. The greatest temperature variation is noted in the upper 10 cm whereas the least variation over the season occurs at 2.25 m. From September through to May, the solum is cooling to temperatures at or below

0°C. The results indicate that the mean annual soil temperature at this site is below 8°C.

The morphological and chemical characteristics of the soil profile under study are typical for Luvisolic soils in Alberta. The profile possesses many of the characteristics of the Breton series however it is very deeply leached; lime is not present to a depth of 2.25 m and argillans are numerous and well developed at this depth. Since the site is located on the upper edge of a deep creek valley, the deep leaching of the profile can be attributed to strong recharge. It is probable that clay and some ionic constituents have been completely removed from the solum to the groundwater.

Analysis of the soil profile clearly indicates that the process of lessivage is predominant in the genesis of this soil. Fine clay sized smectite and to a lesser extent mica have been eluviated from the A horizons and illuviated into the Bt and BC horizons. The zone of maximum clay accumulation is in the the Bt horizons, however, argillans are more numerous and better developed in the BC horizons. It is thought that pedoturbation in the upper horizons may have disrupted and mixed argillans into the soil matrix. Concentrations of clay were noted in the soil matrix and are thought to be the remains of argillans in an intermediate stage of mixing. Fluctuations of soil moisture and temperature are much greater in the Bt horizons than in the BC horizons. Wet-dry and freeze-thaw cycles are responsible for the opening and closing of cracks and pores and the physical mixing of soil materials. This higher clay content of the Bt horizons is

also attributed in part to weathering of fine textured bedrock materials.

Argillans from the upper Bt horizon were noted to have a very micaceous appearance in thin section. They were found to have higher K contents than argillans from BC horizons. An analysis of the colloidal material indicated that mica was the dominant clay mineral migrating from the Ae horizon into the Bt horizon. Since leachates from the Bt lysimeter rarely contained colloidal material, it can be concluded that under present day conditions, mica is illuviated in the upper Bt horizon resulting in the micaceous appearance of the argillans. These findings also suggest that fine clay sized smectite migrated into the lower solum during an earlier stage of soil genesis, possibly under different climatic conditions.

Under present day conditions lessivage is accompanied by the movement of Fe, Al, and organic constituents in solution and in colloidal form into the Bt horizon. The presence of these elements is thought to be a result of weathering of minerals in the Ae horizons. The variability in concentration of these elements in lysimeter samples can be attributed to the rate of water movement through the soil. Rapid water movement does not permit an equilibrium between leaching water and soil materials to occur. Slow water movement does allow for equilibrium to occur resulting in higher concentrations of Fe and Al in solution and in colloidal form. The concentrations of other cations do not appear to be affected by the rate of water movement.

X-ray diffraction analysis of clays from the Ae horizon

indicates that the minerals are quite crystalline. This means that the weathering regime is not intense enough to disrupt crystal structures. It must be that the presence of Fe and Al in solution is a result of the removal of these elements from the external surfaces of clay minerals.

Concentrations of Si in leachates are low suggesting that Si remains in the Ae horizon as amorphous mineral compounds. These may result in the presence of siliceous coatings and the ashy appearance of the Ae horizon.

It is apparent that organic constituents play a significant role in the weathering of clay minerals in the Ae horizon and in the transport of Fe and Al in solution. The concentration of Al in lysimeter leachates is very high given the solubility of Al at near-neutral pH values. The only explanation for this is that Al in solution is complexed with organic constituents. Organic acids are known to be effective in removal of cations from mineral structures and the results of this study suggest that weathering of minerals in the Ae horizon can be attributed in part to the presence of organic constituents.

Analysis of the leachates revealed the presence of variable concentrations of polyphenols, polyuronides, and polysaccharides in solution. The colloidal material also contained organic compounds as indicated by $Na_4P_2O_7$ and H_2O_2 treatment. Changes in pH independent charge following $Na_4P_2O_7$ treatment indicated that bonding between clays and the organic fraction did occur during clay migration. There is no evidence to suggest that the clay-organic interaction is responsible for the initial mobilization

of clay.

On the basis of the foregoing investigation, the following conclusions can be drawn for the soil under study:

1. Under present day conditions, micaceous clays are migrating from the Ae into the upper Bt horizon. These clays are complexed with organic constituents but there is no evidence that organic compounds are responsible for the initial peptization of clay.
2. Lessivage is accompanied by the migration of Fe, Al, and organic compounds and silt size minerals along with clay.
3. While micaceous clays are mobile under present day conditions, fine clay sized smectite has migrated into the Bt and BC horizons during earlier stages of genesis.
4. Heavy prolonged rainfall is necessary for the movement of colloidal material into the lower Bt and BC horizons.
5. The pH of canopy drip and of leaching solutions is close to neutrality.
6. The rate of water movement through the profile significantly affects the concentrations of Fe and Al but not the concentrations of other cations.
7. The presence of Fe and Al in leaching solutions is a result of weathering of minerals in the Ae horizon. It is thought that organic compounds play a significant role in the removal of Fe and Al from the external surfaces of clay minerals.

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APPENDIX A.

X-ray diffraction patterns
of the clay size fraction
of the soil profile.

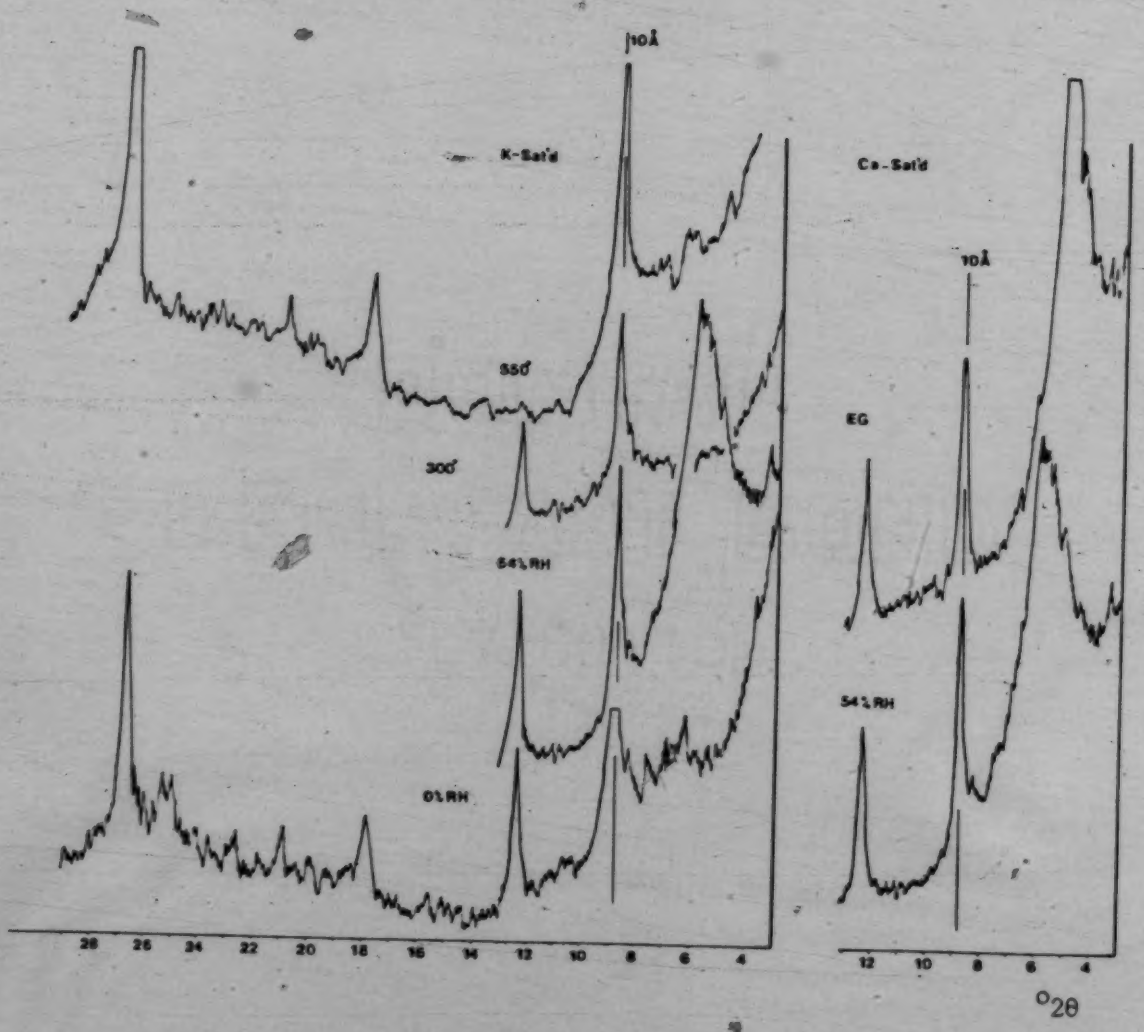

Figure 1. Typical X-ray diffractogram of the total clay size fraction of the Ae horizon.

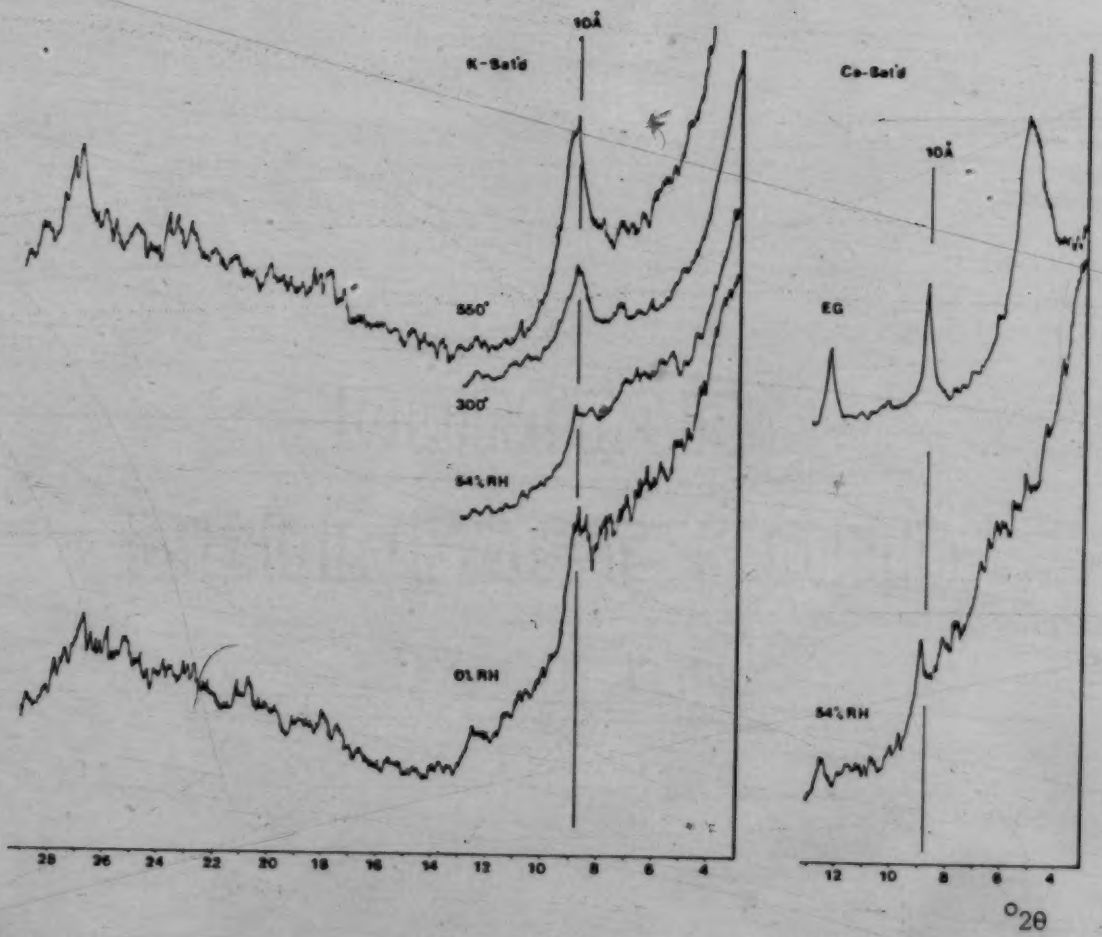

Figure 2. Typical X-ray diffractogram of the fine clay size fraction of the Ae horizon.

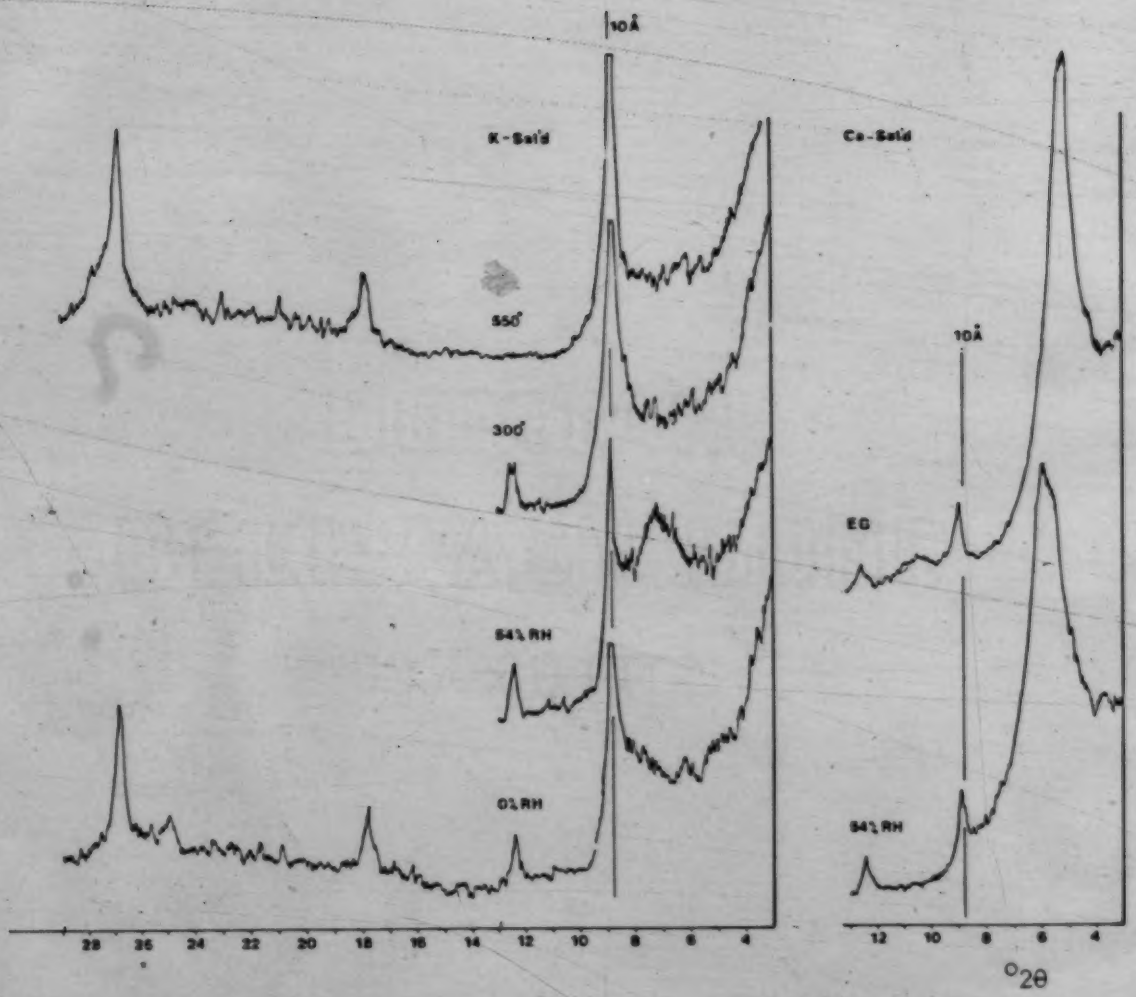

Figure 3. Typical X-ray diffractogram of the total clay size fraction of the Bt horizon.

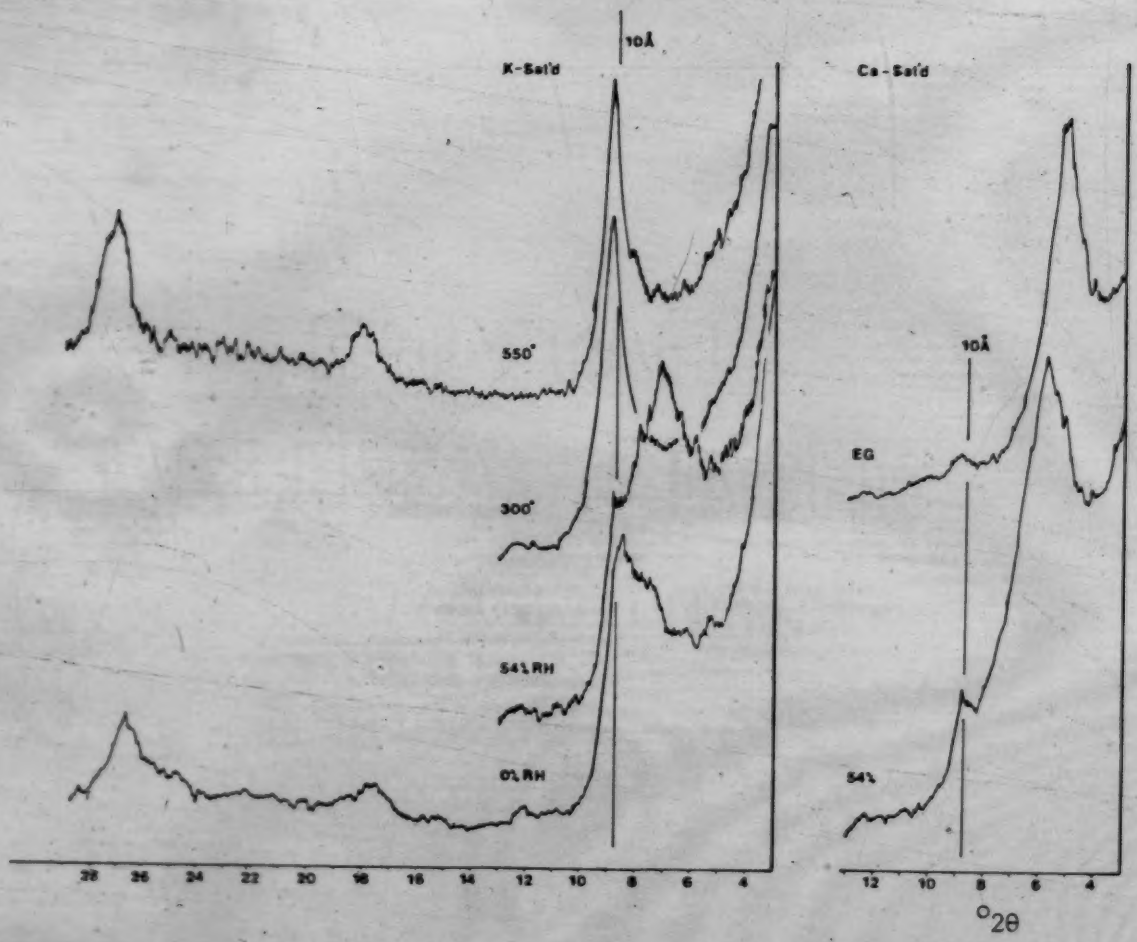

Figure 4. Typical X-ray diffractograms of the fine clay size fraction of the Bt horizon.

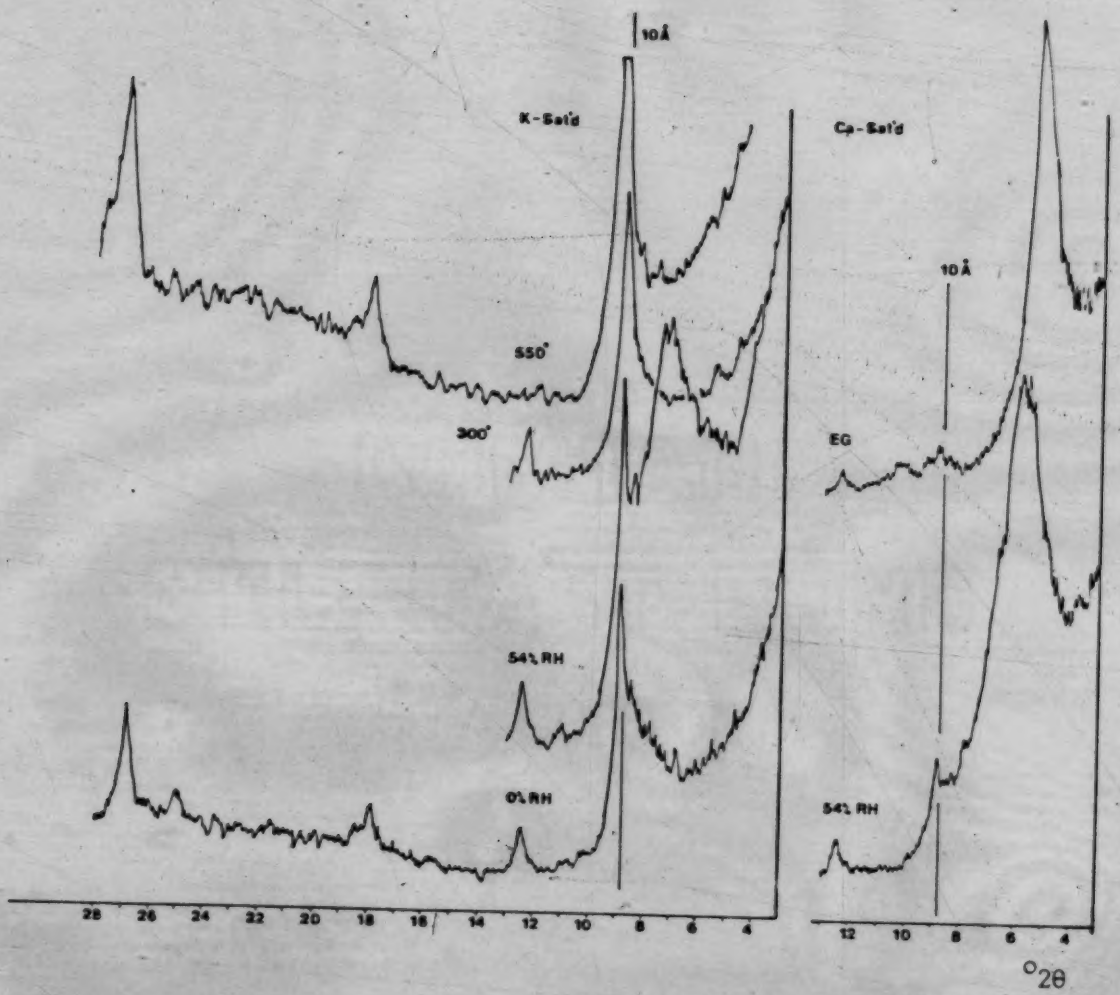

Figure 5. Typical X-ray diffractogram of the total clay size fraction of the BC horizon.

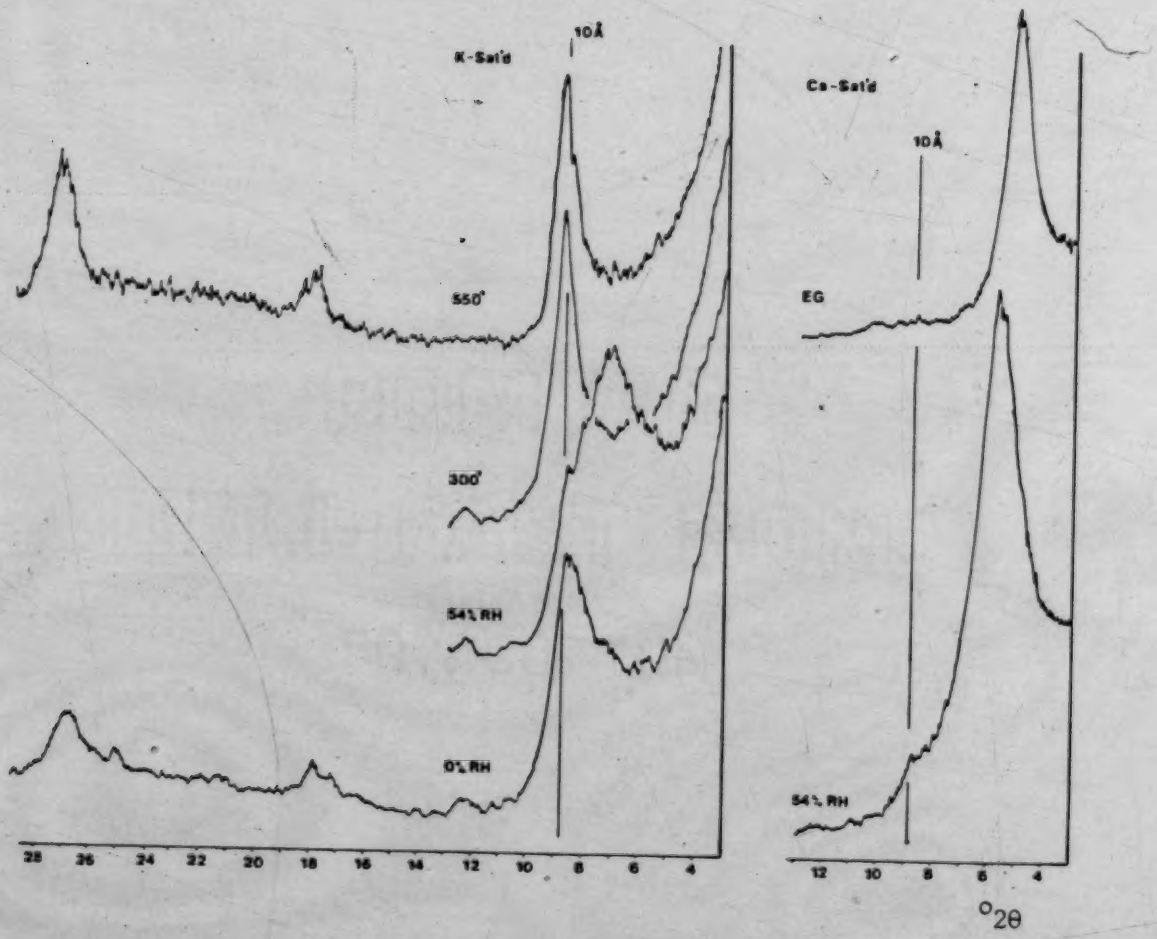

Figure 6. Typical X-ray diffractogram of the fine clay size fraction of the BC horizon.

APPENDIX B.

Micromorphology.

APPENDIX B - MICROMORPHOLOGY

LF — Phytohumigranic. Dominantly fecal pellets ranging in size from 0.1 mm to 1.2 mm. Relatively undecomposed plant remains of variable size and shape are present.

H — Phytohumigranic-granoidic. Fecal pellets are coalesced into units 0.2 mm^2 to 0.5 mm^2. Some plant parts are identifiable however much of the organic matter is humified into black amorphous chunks of variable size and shape.

Aeh — Humigranoidic with a pocket of vuggy porphyric. Granoidic units are composed of mineral material and opaque humified organic material. Pedotubules are filled with granic units. Plasmic fabric is silasepic.

Ae1 — Weakly banded granoidic. Banding varies from 0.4 to 1.0 mm and show a density gradation. Iron nodules are common and are irregular in shape with sharp boundaries. Skeleton grains, dominantly quartz, occupy 25 - 30% of a typical field. Pedotubules are filled with phytogranic units. Plasmic fabric is silasepic.

Ae2 — Banded fragmic-fragmoidic. Bonding varies from 1 mm to 3 mm, the thicker bands being found in the lower portion of the horizon where some isoband structure

is found. Skeleton grains, dominantly quartz, occupy 25 - 30% of a typical field. Iron nodules are common, with irregular shape and sharp boundaries.

AB — Metafragmoidic with areas of fragmic. Numerous joint and skew planes separate units. Iron nodules are less common than in the Ae horizon. Skeleton grains occupy only 10 - 15% of a typical field. Occasional quartzite grains and lithoclasts of siltstone and sandstone are also present. Pedotubules exhibit granic to granoidic structure with some phytogranic units. Plasmic fabric is sepic.

Bt1 — Fragmoidic-porphyric. Pedotubules are common and exhibit granic-granoidic structure with inclusions of phytogranic units (fecal pellets and roots). Occasional, thin, discontinuous argillans may be found in vughs. Iron nodules and lithoclasts of siltstone and sandstone are found but are not common.

Bt2 — Fragmoidic-porphyric. Large pedotubules in the lower portion of this horizon, exhibit granoidic structure. Smaller pedotubules show granic-granoidic structure with inclusions of phytogranic units. Argillans are common but not ubiquitous. They are relatively thin (0.1 mm), discontinuous, and sometimes contain silt grains. Argillans are rarely found in joint or skew planes. They are generally found in vughs. Lithoclasts of siltstone and sandstone are common.

is found. Skeleton grains, dominantly quartz, occupy 25 - 30% of a typical field. Iron nodules are common, with irregular shape and sharp boundaries.

AB — Metafragmoidic with areas of fragmic. Numerous joint and skew planes separate units. Iron nodules are less common than in the Ae horizon. Skeleton grains occupy only 10 - 15% of a typical field. Occasional quartzite grains and lithoclasts of siltstone and sandstone are also present. Pedotubules exhibit granic to granoidic structure with some phytogranic units. Plasmic fabric is sepic.

Bt1 — Fragmoidic-porphyric. Pedotubules are common and exhibit organic-granoidic structure with inclusions of phytogranic units (fecal pellets and roots). Occasional, thin, discontinuous argillans may be found in vughs. Iron nodules and lithoclasts of siltstone and sandstone are found but are not common.

Bt2 — Fragmoidic-porphyric. Large pedotubules in the lower portion of this horizon, exhibit granoidic structure. Smaller pedotubules show granic-granoidic structure with inclusions of phytogranic units. Argillans are common but not ubiquitous. They are relatively thin (0.1 mm), discontinuous, and sometimes contain silt grains. Argillans are rarely found in joint or skew planes. They are generally found in vughs. Lithoclasts of siltstone and sandstone are common.

Plasmic fabric is misepic.

Bt3 Vuggy porphyric with developed joint and skew planes. Argillans are more numerous, thicker (0.2 mm) and more continuous than in the Bt2 horizon. They also may contain silt grains. Argillans are not found in pedotubules or along joint planes, they occur in vughs. Pedotubules are less common, and exhibit granic-granoidic structure except for one very large pedotubule which exhibits poorly accommodated metafragmoidic structure with phytogranic units. Sandstone and siltstone lithoclasts are common and may show inclusions of weathered mica. Plasmic fabric is misepic.

BC1 Vuggy porphyric with developed joint and skewplanes. A zone of meta fragmoidic structure with horizontal isoband structure is thought to be a large pedotubule. Smaller pedotubules exhibit granic-granoidic structure with occasional phytogranic units. Argillans are common and show strong continuous orientation with sharp boundaries. They are found in vughs and rarely in planar voids or pedotubules. Silt grains are often imbedded in argillans. Lithoclasts are common in this horizon and may be fractured with argillans developed in the cracks. Plasmic fabric is misepic.

BC2 Vuggy porphyric. Joint and skewplanes are present in

this horizon but are not as well developed as in upper horizons. Argillans are abundant, occuring in 80 - 90% of the voids. They are thick (0.2^{+} mm), show strong continuous orientation and sharp boundaries. They may be found in some planar voids and pedotubules. Pedotubules are less common than in the Bt horizon. They exhibit granic-granoidic structure with occasional phytogranic units. Lithoclasts are common and are dominantly siltstone with some sandstone present. Plasmic fabric is misepic.

BC3 Vuggy porphyric. Argillans are abundant in this horizon occupying 90% of void surfaces. They show strong continuous orientation, sharp boundaries and imbedded silt grains. Lithoclasts are abundant occupying 25% of a typical field. They are siltstone with some sandstone present and may be quite large. Pedotubules are not as common as in upper horizons, however exhibit similar structure. Plasmic fabric is misepic.

APPENDIX C.

X-ray diffraction patterns
of colloidal leachates
following each set of treatments.

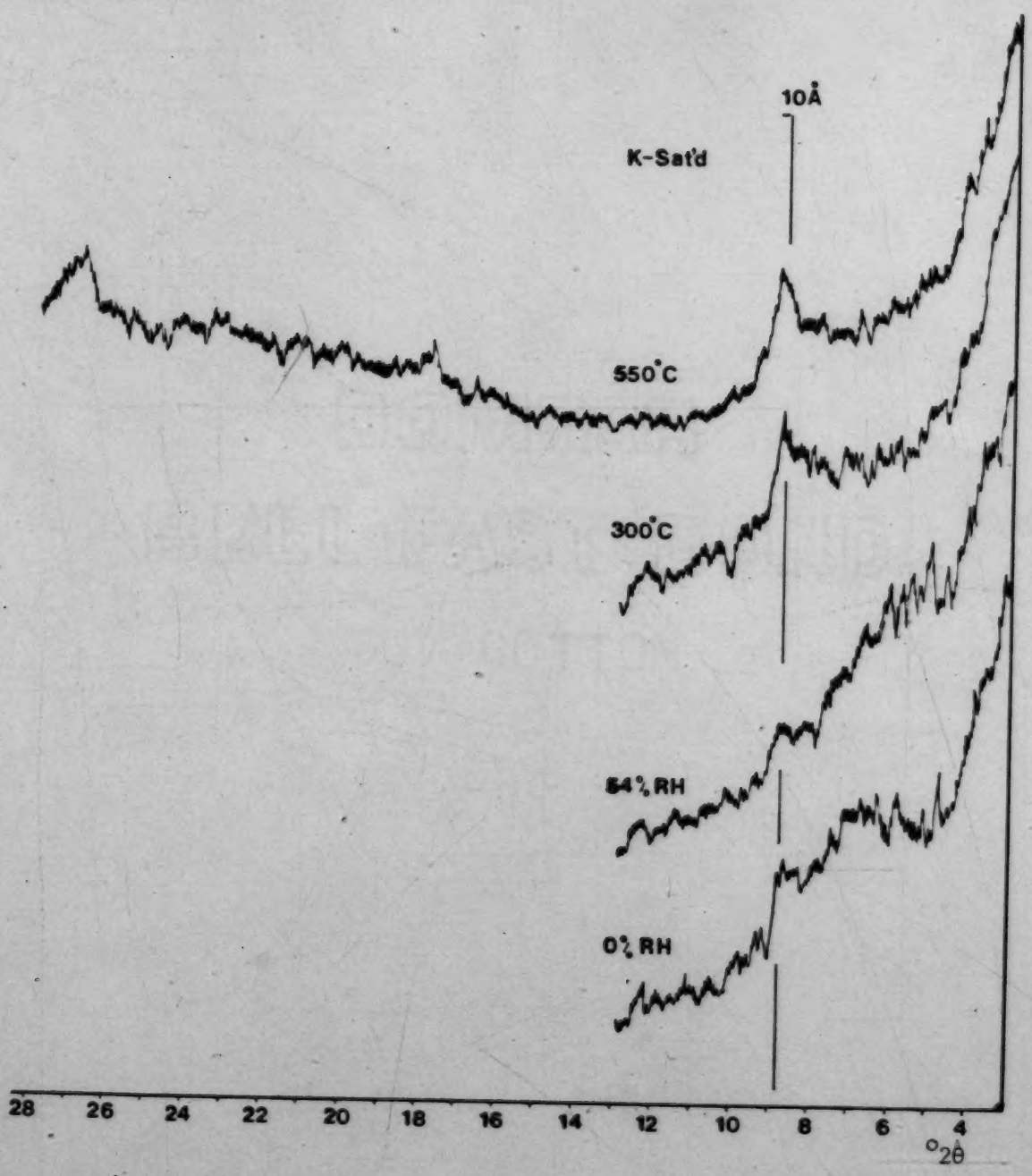

Figure 7. X-ray diffractogram of the untreated 1977 colloidal material.

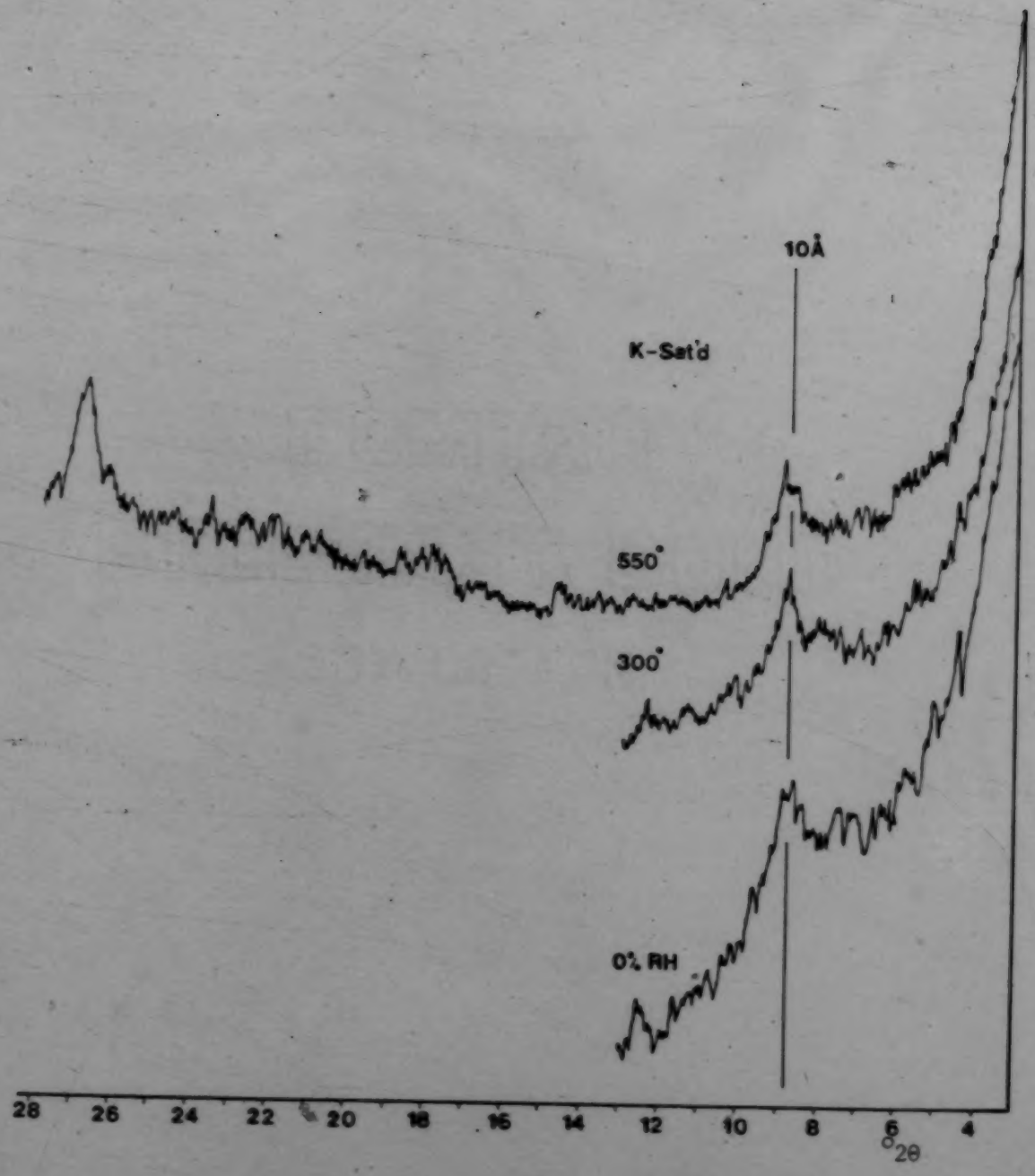

Figure 8. X-ray diffractogram of the 1977 colloidal material following pH independent charge determination.

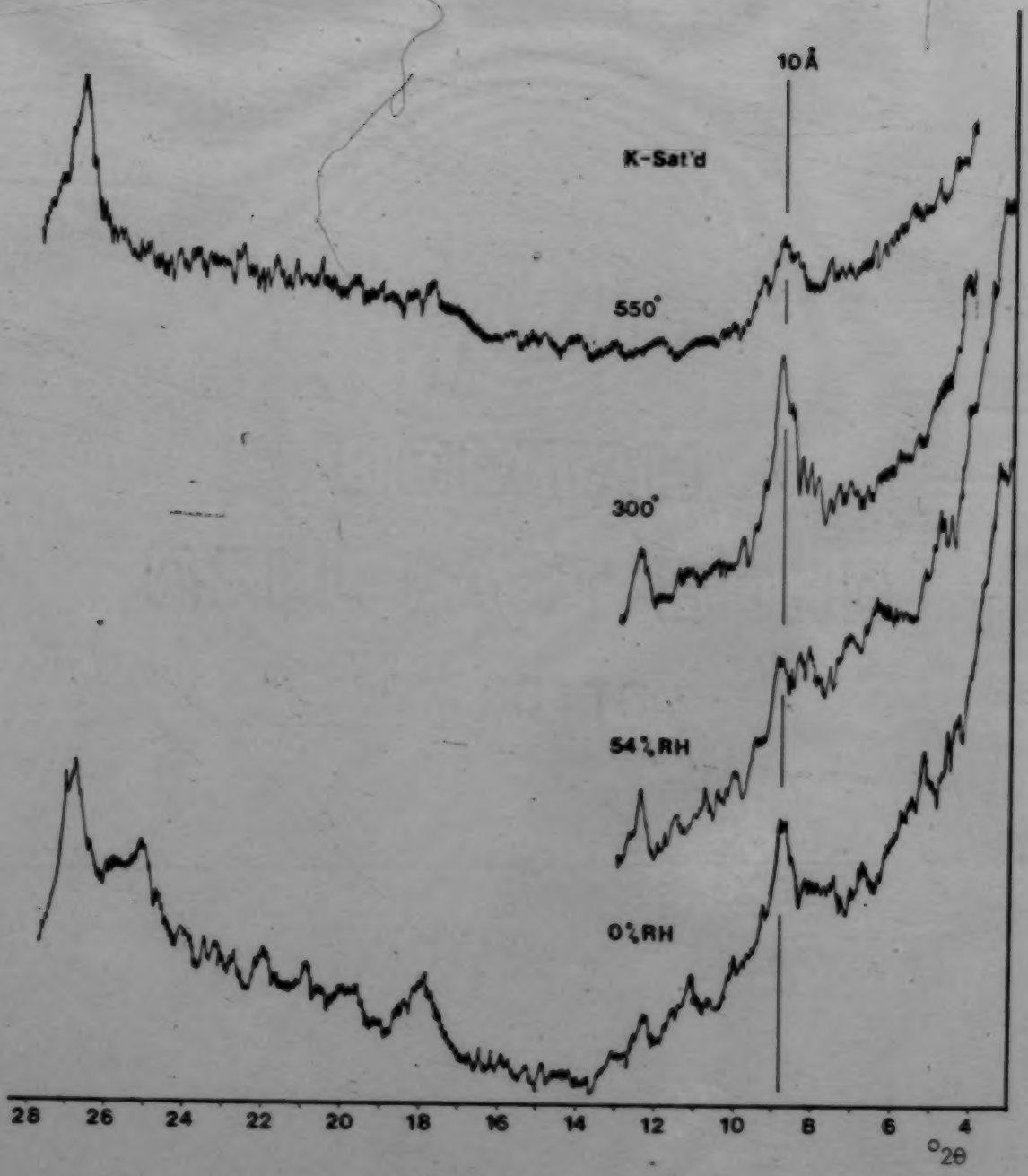

Figure 9. X-ray diffractogram of the 1977 colloidal material following $Na_4P_2O_7$ treatment.

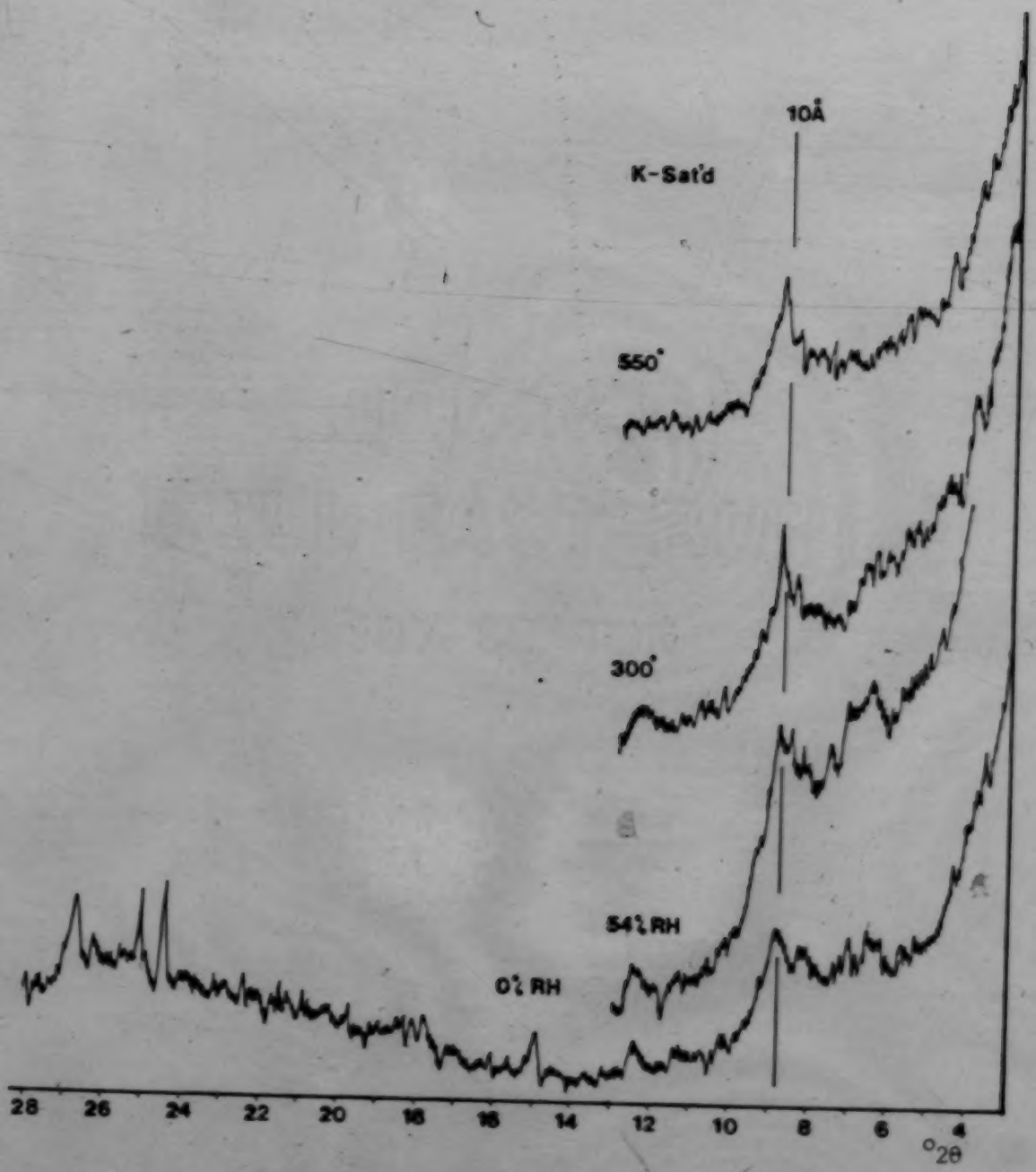

Figure 10. X-ray diffractogram of 1977 colloidal material following acid ammonium oxalate treatment.

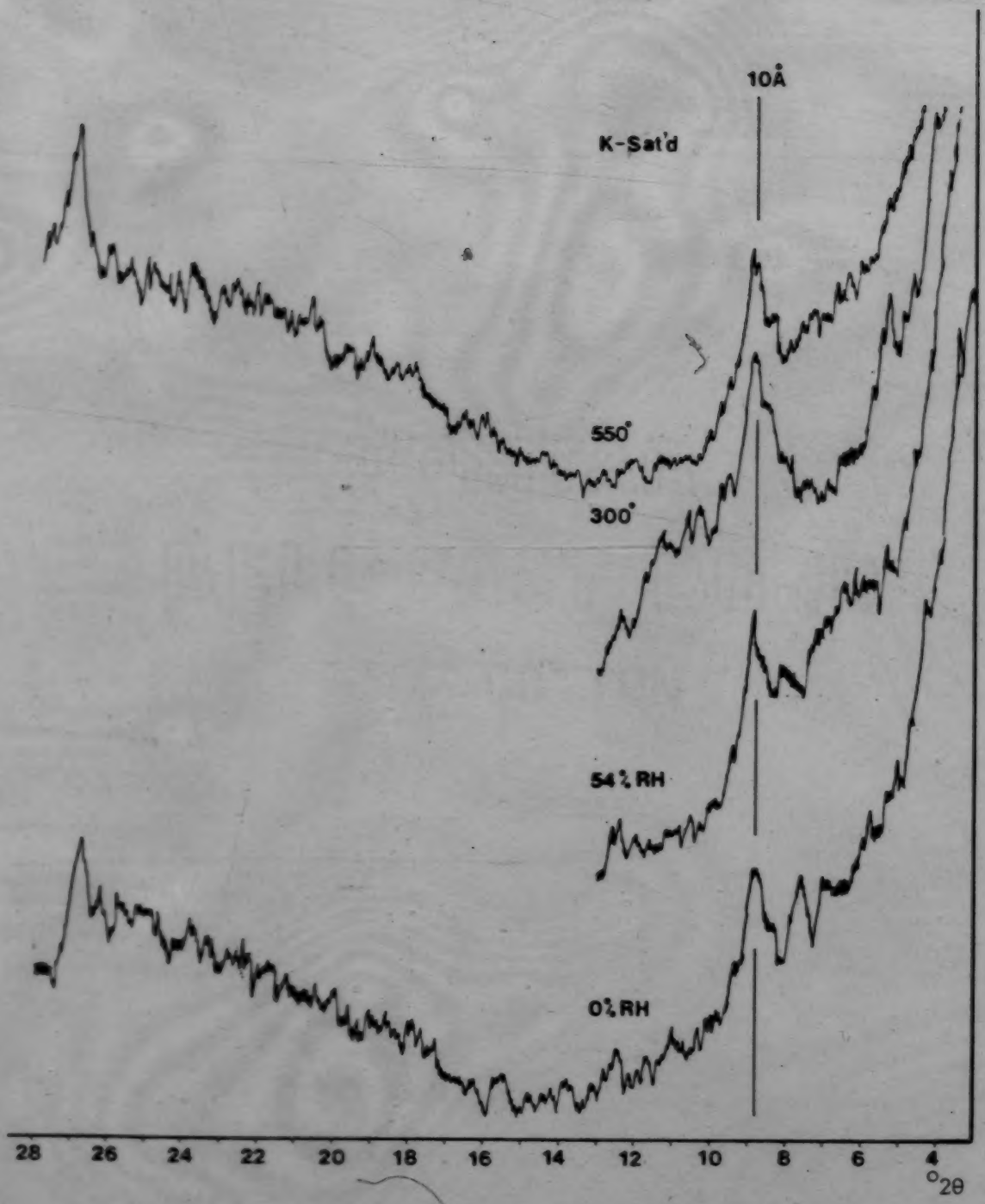

Figure 11. X-ray diffractogram of 1977 colloidal material following sodium citrate treatment.

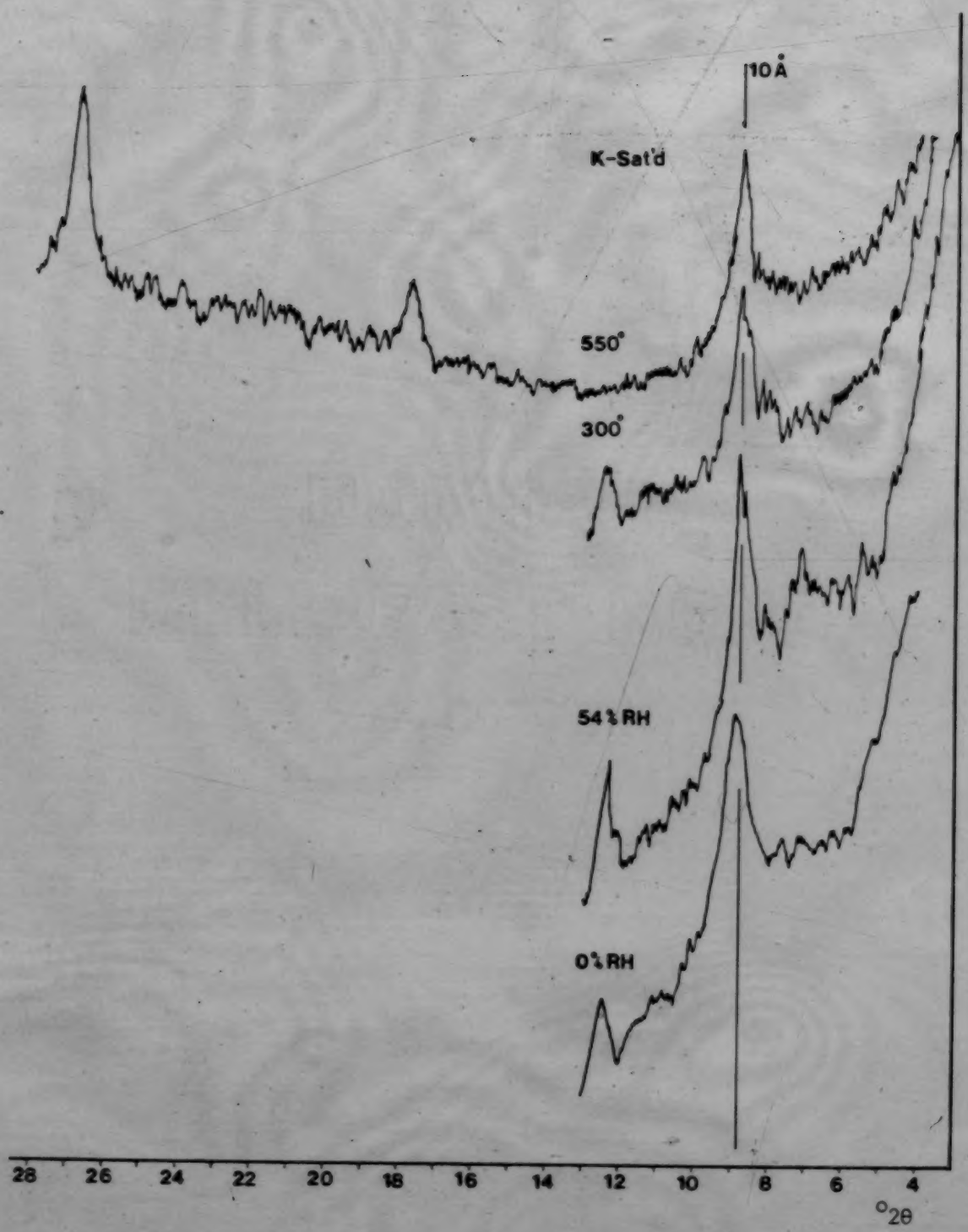

Figure 12. X-ray diffractogram of 1977 colloidal material following H_2O_2 treatment.

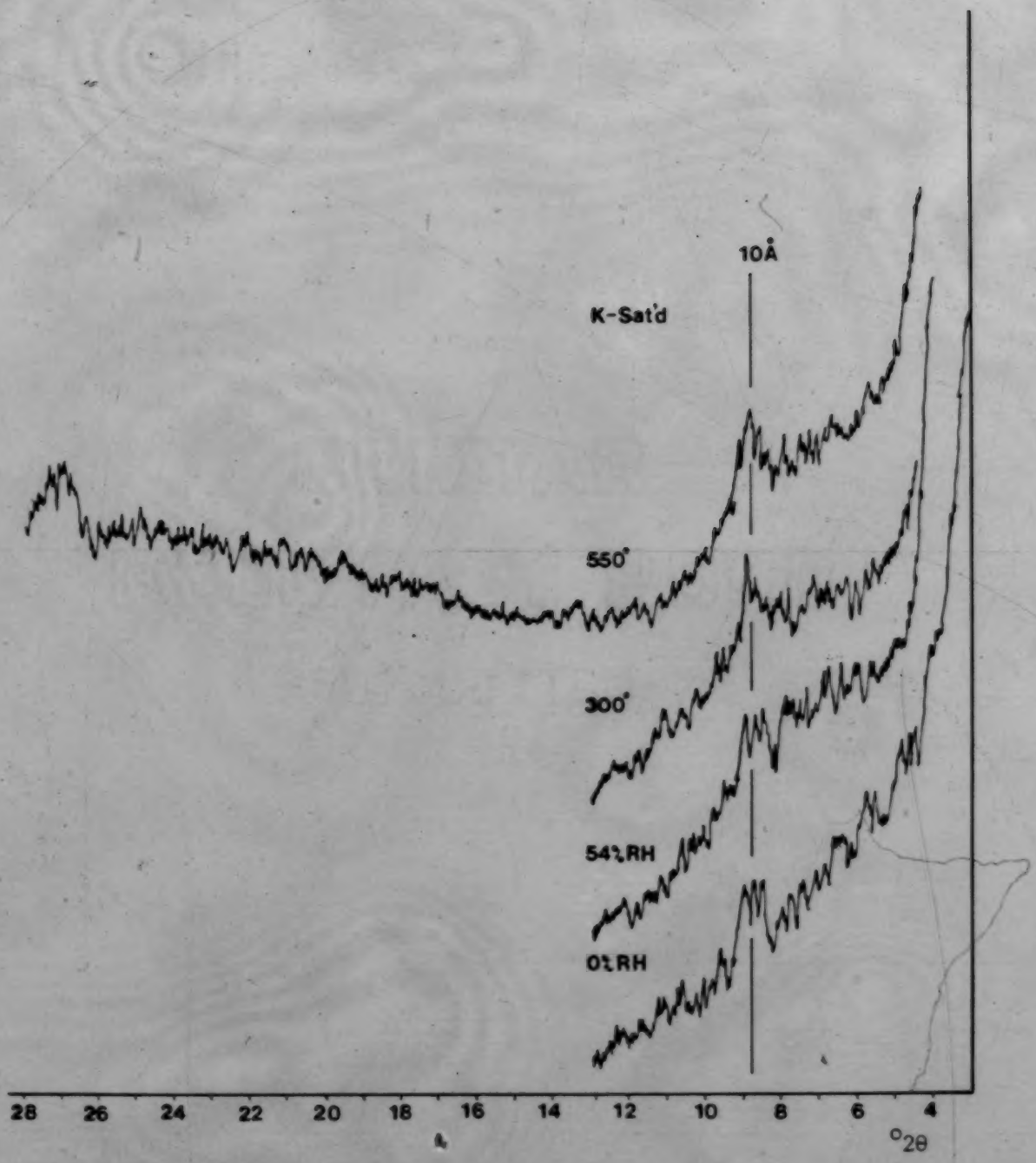

Figure 13. X-ray diffractogram of the A fraction of the 1978 colloidal material following pH independent charge determination.

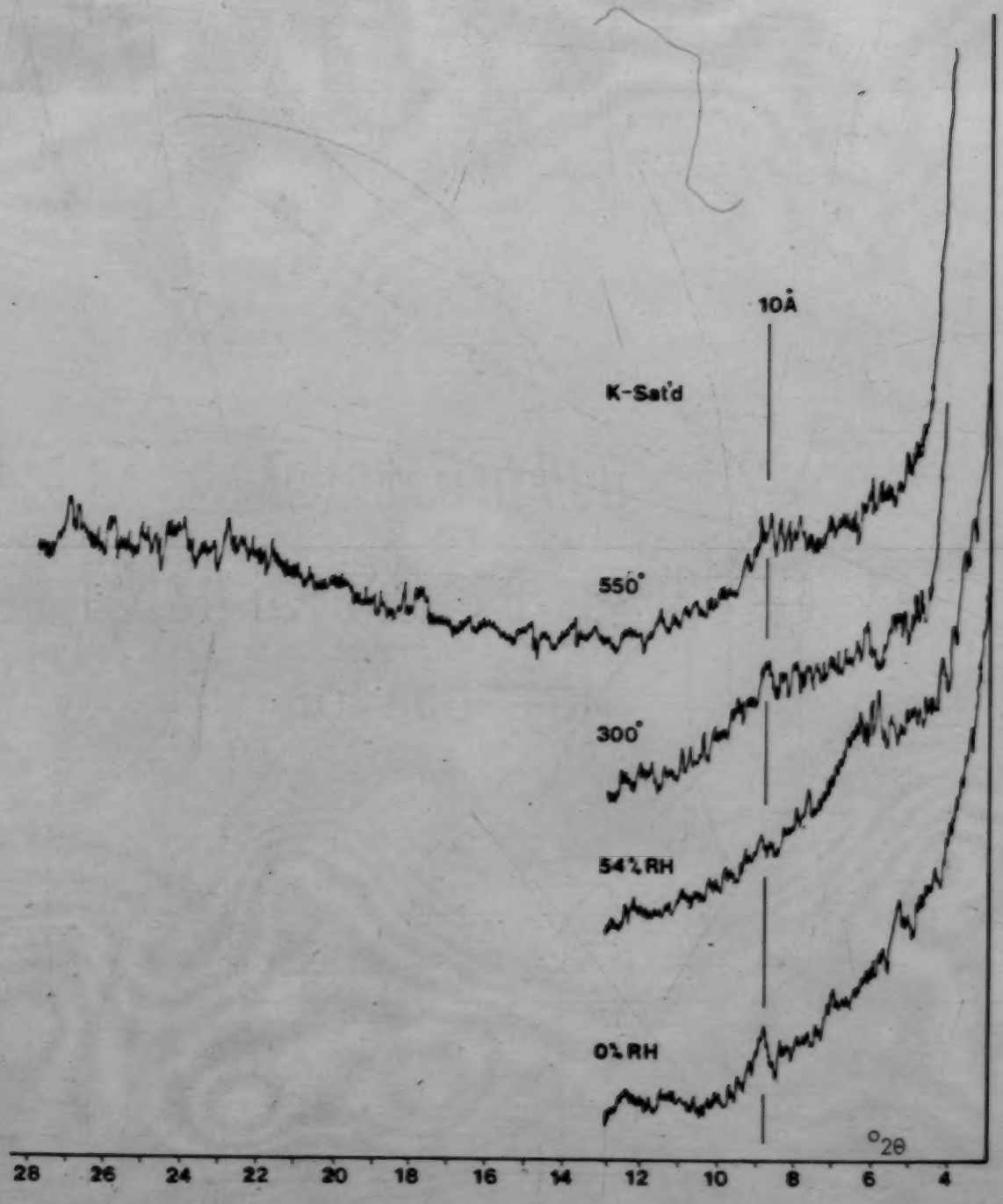

Figure 14. X-ray diffractogram of the A fraction of the 1978 colloidal material following $Na_4P_2O_7$ treatment.

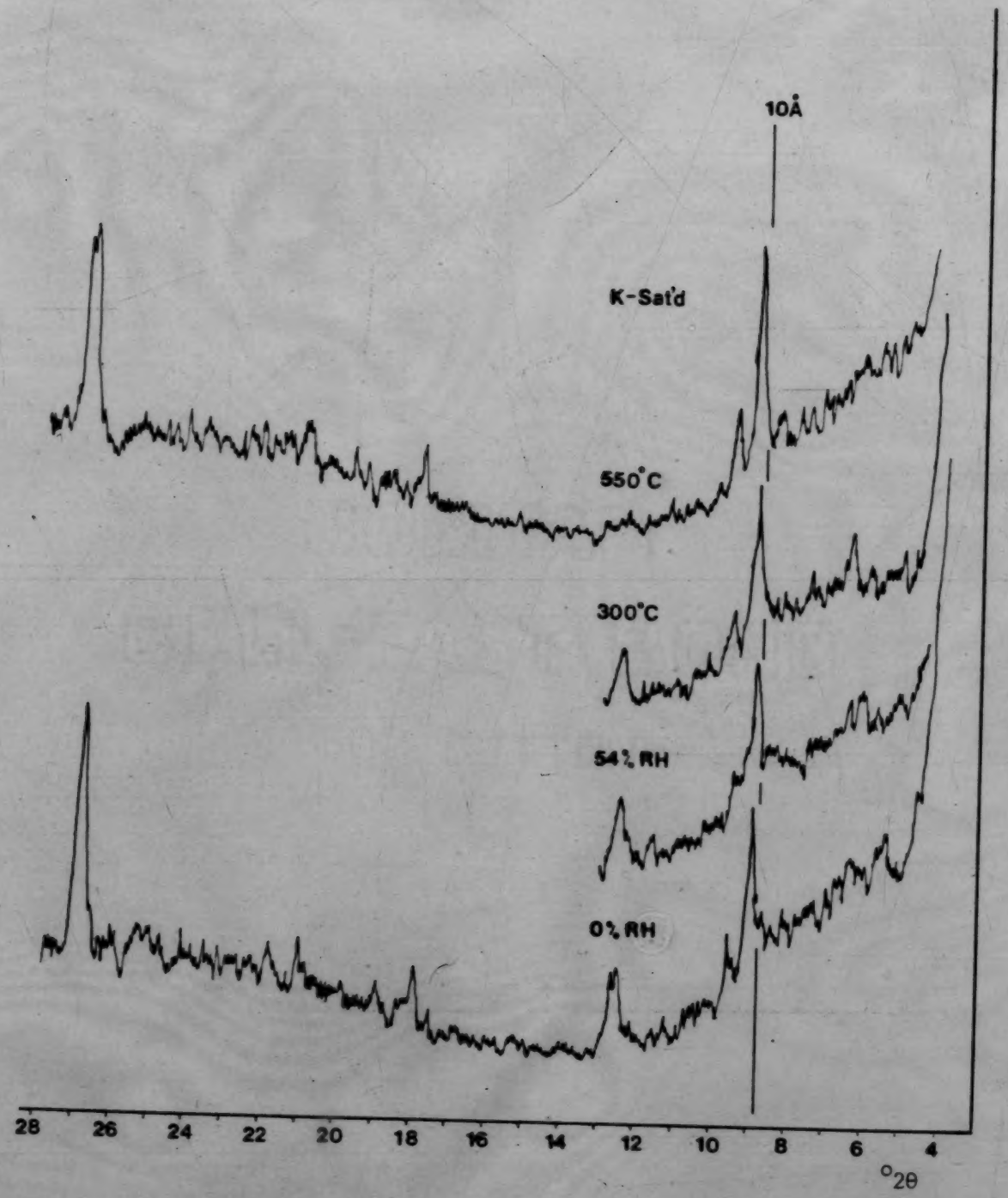

Figure 15. X-ray diffractogram of the A fraction of the 1978 colloidal material following H_2O_2 treatment.

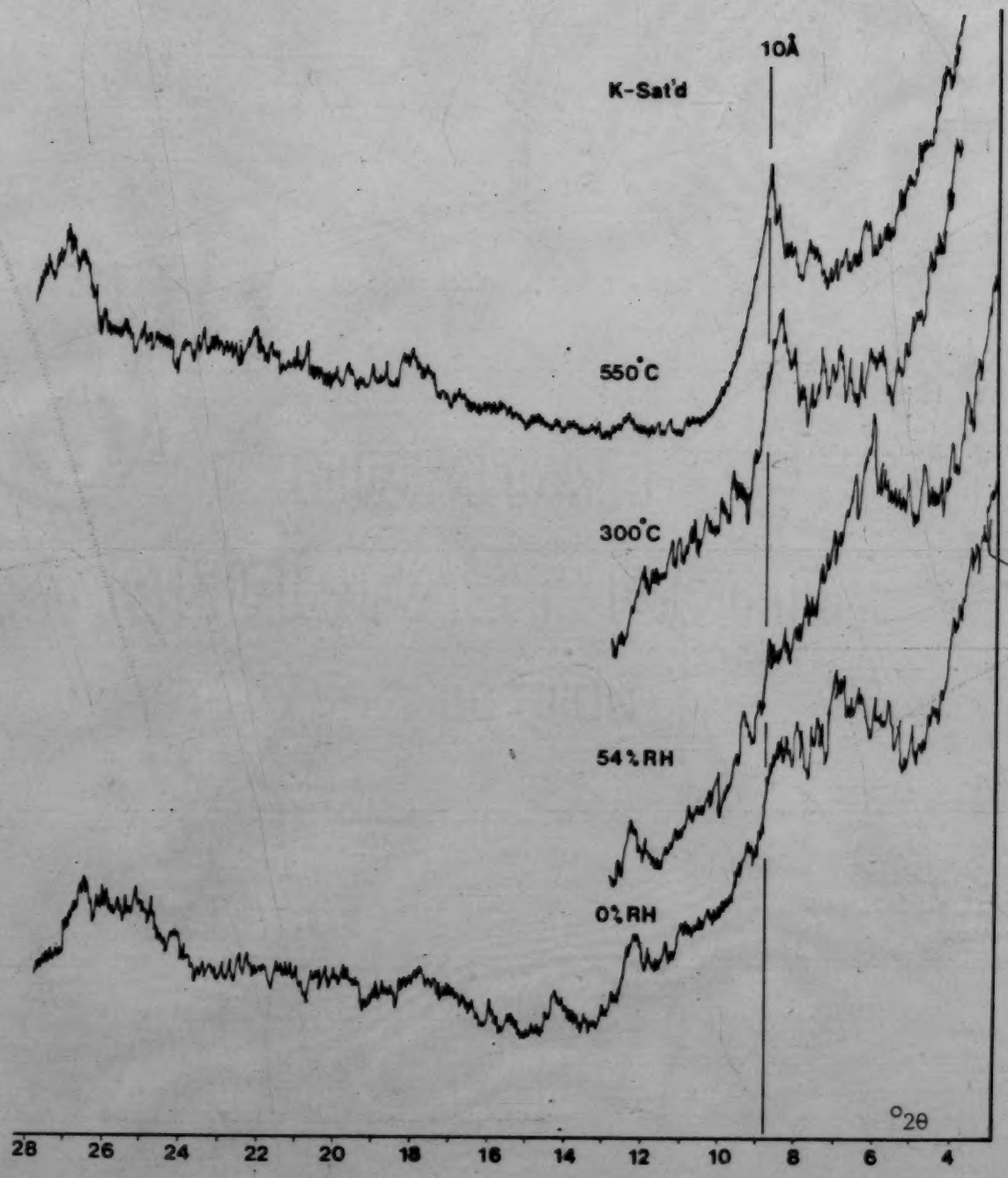

Figure 16. X-ray diffractogram of the B fraction of the 1978 colloidal material following pH independent charge determination.

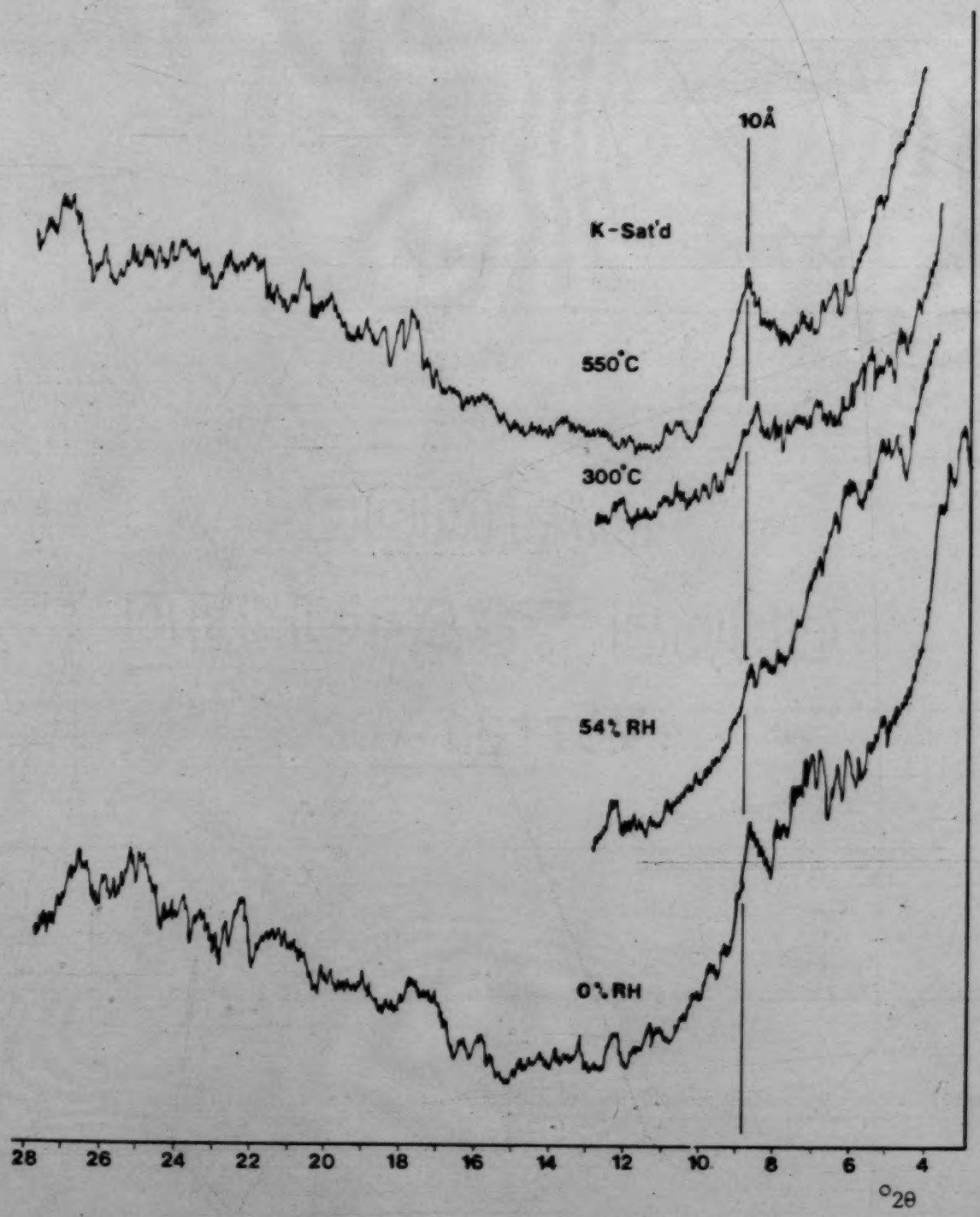

Figure 17. X-ray diffractogram of the B fraction of the 1978 colloidal material following $Na_4P_2O_7$ treatment.

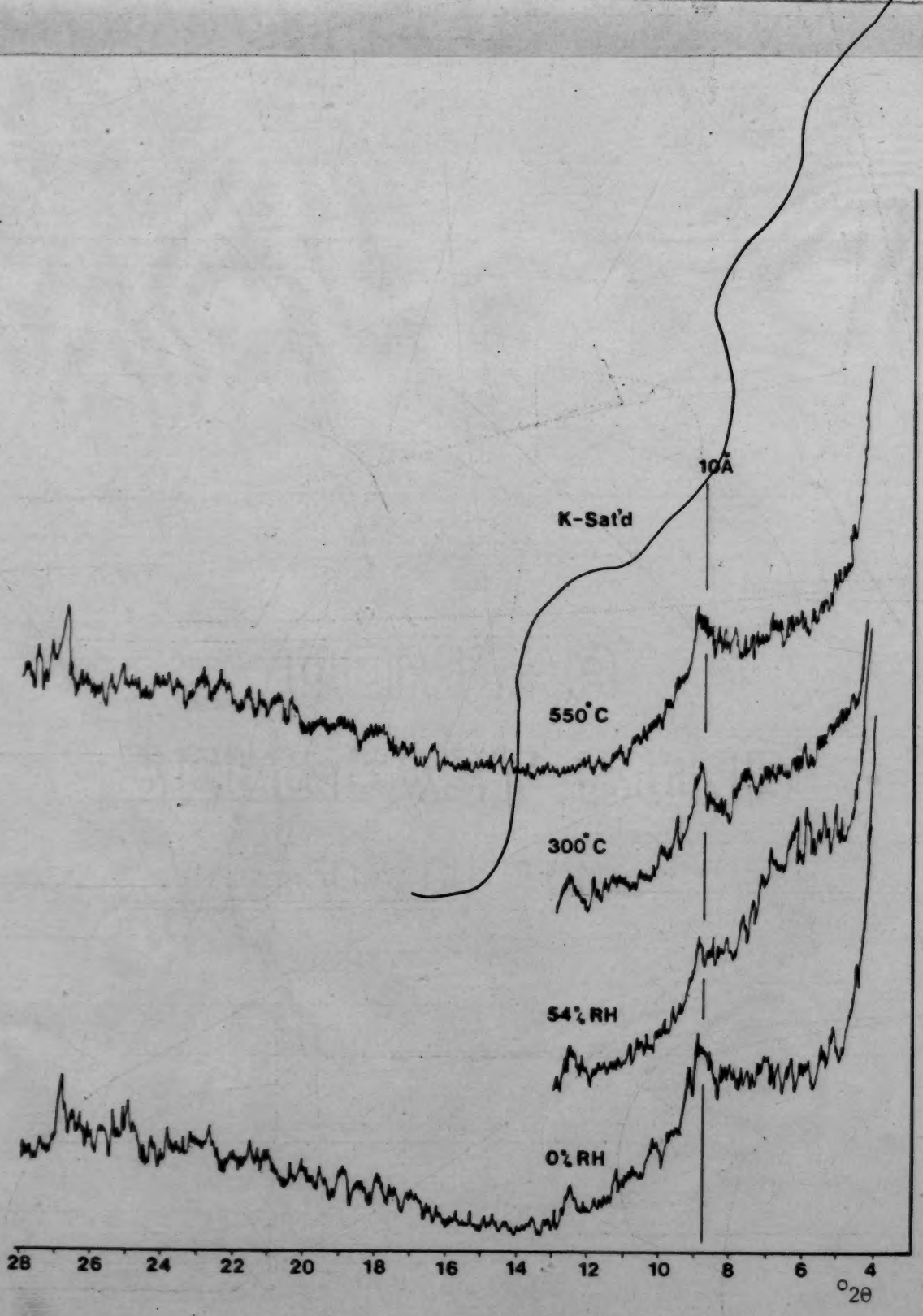

Figure 18. X-ray diffractogram of the B fraction of the 1978 colloidal material following H_2O_2 treatment.

APPENDIX D.

Soil moisture and temperature data.

Table 1. Weekly soil moisture and precipitation 1977.

Horizon	LFH	Ae	Bt	BC1 (90 cm)	BC2 (225 cm)	Precipitation (mm)
May 20	–	20	32	–	20	–
May 27	116	19	30	–	20	–
June 3	126	19	34	–	29	–
June 10	94	18	32	–	26	–
June 17	163	17	30	–	24	–
June 24	67	13	26	32	23	8.4
June 30	54	10	22	32	22	4.3
July 8	148	20	25	32	21	22
July 15	129	20	28	32	21	–
July 22	107	18	28	32	21	15
July 29	154	12	22	32	21	23
Aug 5	122	16	22	32	21	32
Aug 12	200	19	22	32	21	–
Aug 19	122	16	22	32	21	24
Aug 26	200	16	21	31	21	–
Sept 3	139	20	35	31	21	–
Sept 8	104	19	34	31	21	2
Sept 16	129	18	34	31	21	7
Sept 23	112	17	32	31	21	16
Sept 30	139	18	30	31	21	–
Oct 7	104	18	29	31	21	–
Oct 14	92	17	29	31	21	–
Oct 21	60	17	28	31	21	–
Oct 28	–	16	27	31	21	–
Nov 4	38	15	26	31	21	–
Nov 11	38	15	25	31	21	–
Nov 18	32	15	24	31	21	–

Table 2. Weekly soil moisture conditions and precipitation 1978.

Horizon	LFH	Ae	Bt	BC1 (90 cm)	BC2 (225 cm)	Precipitation (mm)
April 10	200	19	17	30	21	2
April 17	154	20	18	30	21	3
April 24	139	18	18	29	21	6
May 1	119	19	26	30	21	5
May 8	116	19	28	30	21	9
May 14	107	18	28	30	21	7
May 23	94	18	29	30	21	22
May 28	129	19	29	30	21	23
June 4	101	19	31	32	22	22
June 11	92	18	31	32	23	6
June 15	139	19	29	32	22	27
June 23	101	18	30	32	23	17
June 30	154	20	33	32	25	22
July 7	59	15	28	32	25	4
July 14	113	19	29	32	26	34
July 21	61	15	24	32	26	4
July 28	154	13	18	32	26	18
Aug 3	70	12	17	32	26	1
Aug 10	43	10	–	31	25	0.5
Aug 17	200	10	–	28	24	26
Aug 24	200	10	–	28	24	–
Aug 31	90	15	17	27	24	–
Sept 7	56	12	17	28	24	7
Sept 15	200	22	27	27	24	57
Sept 22	129	20	33	25	24	28
Sept 29	200	19	31	25	25	9
Oct 6	122	19	31	21	24	5
Oct 13	96	18	30	23	24	1
Oct 20	200	17	29	23	24	–
Oct 25	154	18	29	23	24	7
Nov 1	119	17	28	22	24	1
Nov 8	200	20	29	22	24	23

Table 3. Mean monthly soil moisture and precipitation 1978.

Horizon	April	May	June	July	Aug	Sept	Oct	Nov
F	173.3	113.0	117.4	96.8	120.6	146.3	143.0	160
Ae	18.6	18.8	18.6	15.3	11.6	18.3	17.9	18.5
Bt	17.8	27.8	30.9	24.6	17	27.3	29.7	28.5
BC1 (90 cm)	30.0	30.4	26.5	32	29.3	26.5	22.4	22.0
BC2 (225 cm)	21.7	21.2	23.3	25.7	27.3	24.4	24.2	24.1
Precipitation (mm)	12.1	32.3	95.3	59.4	26.9	98.5	6.0	29.6

Table 4. Mean monthly soil moisture and precipitation 1977.

Horizon	May	June	July	Aug	Sept	Oct	Nov
F	116	88	134	161	125	86	36
Ae	19.9	15.9	17.4	16.9	19.5	17.1	15.3
Bt	30.6	27.0	25.6	22.0	33	28.2	25.1
BC1 (90 cm)	-	32	32	32	31.3	31.0	31
BC2 (225 cm)	20.5	20.7	21.3	21.1	21.4	21.4	21.3
Precipitation (mm)	-	54.6	60.0	58.4	23.3	-	-

Table 5. Mean monthly soil temperature at selected depths for 1977.

Depth (cm)	May	June	July	Aug	Sept	Oct	Nov
0	9.5	12.8	14.0	12.4	9.4	3.5	2.3
12.6	6.4	8.8	11.3	11.4	8.2	3.6	0.8
25.3	6.4	8.8	10.8	11.6	8.6	5.2	2.8
38.0	5.6	8.1	10.7	11.3	8.9	5.4	3.2
50.6	5.3	7.7	9.6	10.7	8.8	5.8	3.2
63.3	5.3	7.3	9.2	10.2	8.7	6.3	4.5
75.9	5.1	7.1	8.8	10.0	8.8	6.6	5.0
88.6	5.1	6.9	8.4	10.0	8.8	7.0	5.4
182.2	3.6	4.9	6.6	7.7	7.8	7.3	6.4

Table 6. Mean monthly soil temperature at selected depths for 1978.

Depth (cm)	April	May	June	July	Aug	Sept	Oct
0	4.5	13.2	16.7	16.0	16.0	10.0	7.1
12.6	0	5.8	11.0	12.8	12.3	10.0	5.8
25.3	0	5.4	10.4	12.7	12.1	10.1	6.7
38.0	0	4.8	9.8	12.4	11.8	10.1	7.0
50.6	0	4.3	9.0	11.3	11.2	9.8	7.3
63.3	0.2	4.0	8.4	10.7	11.0	9.6	7.4
75.9	0.3	3.7	8.0	10.3	10.8	9.6	7.8
88.6	1.0	3.6	7.7	10.1	10.6	9.8	7.7
182.2	1.8	2.4	4.8	7.1	7.6	8.4	7.3